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U.S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 12 MARCH 1934 No. 3

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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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The Bureau of Standards Journal of Research will hereafter carry standard abbreviations in close agreement with the national practice set up in the American Standards Association standard Z10i–1932, abridged by omitting certain terms.

This standard list was formulated by a committee representative of 34 national scientific and technical organizations. The list was formally adopted by the ASA after approval by and recommendation of the five sponsor bodies under whose auspices the project was brought to successful completion. These five national societies, which acted for the 34 scientific and technical groups, are as follows:

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U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP653

Part of Bureau of Standards Journal of Research, vol. 12, March 1934

STATISTICAL INVESTIGATION OF THE UNIFORMITY OF GRADES OF 1,000 LOVIBOND RED GLASSES

By Geraldine K. Walker

ABSTRACT

The need for uniformly graded Lovibond red glasses has long been urgent among those engaged in the vegetable- and cottonseed-oil trade. Huge quantities of oil are yearly bought and sold with color as an important contributing factor in the rules governing the transactions. The grade of the oil depends upon its color and the color is defined in terms of Lovibond glasses. The calibration of these red glasses in terms of the standard unit and scale, known as the Priest-Gibson unit and scale, has been in progress at the Bureau of Standards since 1928. By direct comparison with the working standards a new value or regrade numeral is assigned to each glass submitted for test. The new value is the effective additive value when the glass is used in combination with a 35-yellow (35Y) glass. The direct-comparison method of calibration and the apparatus are described.

The statistical investigation of the data resulting from the calibration of the first 1,000 red glasses shows that variations of a whole unit frequently exist among glasses of similar Lovibond numeral. The several illustrations display in different ways the discrepancies found among these glasses. For purposes of the oil trade, not only should all glasses of the same color bear the same numeral, but, also, those of different colors should bear the corresponding proper numerals according to a scale which is accurately additive. Both regular and erratic departures from additivity have been demonstrated in the Lovibond scale as embodied in these 1,000 red glasses combined with 35Y, and the additive nature of the Priest-Gibson scale has been confirmed.

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I. INTRODUCTION

The standardization of Lovibond red glasses [1] was undertaken at the request [2] of the Society of Cotton Products Analysts, now Ameri-

[1] A description of the Lovibond color scale is given on pages 6 and 7 of "Colour Measurement", a recently published brochure of The Lovibond Tintometer, The British Drug Houses Pattern, Pat. No. 299194. For the method of construction of these scales of red, yellow, and blue glasses, see J. W. Lovibond, Light and Colour Theories, E. & F. N. Spon, London, pp. 29–30.

[2] As early as 1912 an appeal was made by the Society of Cotton Products Analysts to the Bureau of Standards to test Lovibond tintometer glasses (Report of Proceedings of the Fourth Annual Meeting of the Society of Cotton Products Analysts, Chicago, Ill., June 21, 1913). Regarding the work on the standardization of Lovibond glasses prior to 1927, see the prefatory statement by I. G. Priest in a paper by K. S. Gibson and F. K. Harris, The Lovibond Color System—A Spectrophotometric Analysis of the Lovibond Glasses, B.S. Scientific Paper 547, February 1927.

can Oil Chemists' Society, whose members are engaged in the vegetable oil industry. The oil chemists use these red glasses in combination with Lovibond yellow glasses to assign grades to their oil products, the grade and price depending upon the color. Discrepancies [3] were occurring in the grades assigned to the same samples of oil in the laboratories of producer and consumer, where different sets of glasses were in use. Notable inconsistencies between the colors of the red glasses and their Lovibond numerals [4], *N*, were known to exist and it was desired to eliminate as far as possible any differences in the grades of oils due to these inconsistencies. The grade of an oil is defined by two numbers which represent the combination of red and yellow glasses similar in color to the oil. One is the sum of the Lovibond numerals on the red glasses and the other is the Lovibond numeral on the yellow glass used in the combination. In decisions of greatest importance, the red glasses are used in combination with Lovibond 35 yellow (35Y) [5] and it has already been shown [6] that the lack of uniformity among 35Y glasses is relatively unimportant.

Uniformity among the red glasses, however, is an important factor. All glasses of the same color should bear the same numeral, and in addition, since they are usually used in combinations of two or three, those of different color should bear the corresponding proper numerals according to a scale which is accuratively additive. That is, when two or more glasses are used in combination, they should be equivalent [7] to a single glass of numeral equal to the sum of those in the combination. This is called the additivity condition, and by its application a relatively small number of glasses by various combinations may be made to yield the many standards of color needed in grading vegetable oils.

When combined with 35Y, the red glasses failed to meet these conditions to the extent described in the present paper. Furthermore, there was no satisfactory additive scale or set of standards available by means of which the red glasses could be calibrated. The standardization of red glasses has, therefore, consisted of two principal parts:

1. *The standardization of the Lovibond red glasses of the Bureau's own set, designated as B.S. 9940, in combination with Lovibond 35Y.*—The Society of Cotton Products Analysts and the Interstate Cotton Seed Crushers' Association adopted this set as "standard" as early as 1913. The derivation of this required scale, by means of which new numerals, *N''*, satisfying the additivity condition, were assigned to glasses of set B.S. 9940, is described in detail in a paper now in prep-

[3] Some of the possible sources of the discrepancies mentioned in B.S. Scientific Paper 547, p. 10, have been studied and results presented in the following publications:
D. B. Judd and G. K. Walker, A Study of 129 Lovibond Red Glasses with Respect to the Reliability of their Nominal Grades, Oil and Fat Industries, 5, pp. 16–26, January 1928.
I. G. Priest, Tests of Color Sense of A.O.C.S. Members and Data on Sensibility to Change in Lovibond Red, Oil and Fat Industries, 5, pp. 63–73, March 1928.
D. B. Judd, Effect of Temperature Change on the Color of Red and Yellow Lovibond Glasses, B.S. Jour. Research, vol. 1, (RP31), pp. 859–866, November 1928.
I. G. Priest, D. B. Judd, K. S. Gibson, and G. K. Walker, Calibration of Sixty-five 35-Yellow Lovibond Glasses, B.S.Jour. Research, vol. 2 (RP58), pp. 793–819, April 1929.

[4] The numeral engraved on each glass, presumably by the Lovibond establishment, will be represented by *N* and will be referred to in the present paper by use of any one of the terms: Lovibond numeral, nominal grade, or maker's numeral. This Lovibond numeral is nominally a means of differentiating between the colors of the various members of the red scale, which is embodied in 155 red glasses ranging in nominal grade from .01 to 20.0 Lovibond units. A brief but comprehensive description of the Lovibond system has been published in B.S. Scientific Paper 547, p. 11. Similar numerals are used in the Lovibond yellow and blue scales.

[5] Rules governing transactions between members of the National Cottonseed Products Association, Inc. successors to the Interstate Cotton Seed Crushers' Association, Inc. See article 4, rules 60–65.

[6] B.S. Research Paper 58, p. 819.

[7] Their equivalence is considered established if they evoke the same chromaticity under like conditions; see footnote 16, p. 274.

aration.[8] These glasses having N'' values will be referred to as standard glasses.

2. The standardization (regrading) of red glasses submitted to the Bureau for calibration in terms of the standard N'' scale.—This second standardization is the subject of the present paper. The routine method of calibration now used was adopted in the fall of 1927 and the routine testing of red glasses submitted for calibration has been in progress since January 1928. From September 1927 to July 1928 this work was performed in cooperation[9] with the American Oil Chemists' Society. Since that time, the Bureau of Standards has continued the routine grading and in March 1929 the glasses calibrated totaled 1,000.

The present paper describes the apparatus and the procedure used in the calibration of these 1,000 glasses and gives the results of a statistical analysis of their regrade numerals relative to their respective nominal grades.

It may be emphasized that all values of N'' given in this paper refer to the red glasses when combined with 35Y. It is doubtless true that the regrade numerals so obtained for the red glasses would also hold for a considerable range of yellow glasses on both sides of 35Y, but these numerals would not necessarily be valid for the red glasses used alone or with a Lovibond yellow glass of small numeral.

II. STANDARD GLASSES

The method adopted for the routine grading of red glasses is known as a direct-comparison method because a submitted glass is compared directly with a standard glass or combination of standard glasses. For convenience in grading, it was desirable to have as standards a series of glasses ranging in Priest-Gibson numerals, N'', from 0.1 to 1.0 in multiples of 0.1 and from 1.0 to 10.0 in multiples of 1.0. The selection of certain glasses for standards was, therefore, largely governed by the degree of approximation of their N'' values to these desired multiples. In table 1 are listed the values of N and N'' for those standards of B.S. 9940 which were most extensively used in the calibration of the 1,000 glasses. As already noted, Lovibond 35Y was used in deriving the N'' values of these standards.

TABLE 1.—*Standards of B.S. 9940 used in routine grading of Lovibond red glasses*

N[1]	N''[2]	N	N''
0.02	0.104	2.8	2.99
.13	.199	3.9	3.94
.18	.296	4.9	5.08
.28	.365	6.8	6.85
.38	.495	7.6	7.59
.46	.593	9.0	9.17
.56	.711	9.8	10.00
.64	.806	12.0	12.17
.74	.900	13.0	12.98
.86	1.003	17.0	17.12
1.8	1.95		

[1] N=Maker's numeral.

[2] N''=Regrade numeral in Priest-Gibson units. These values are uncertain in the second decimal place. Nevertheless, they have been used, as given, in the calibration of tested glasses. Lovibond 35Y was used in deriving the N'' values of these standards.

[8] The unit and scale were established by I. G. Priest and K. S. Gibson in May 1927, and a brief description was given orally both at the Convention of the A.O.C.S. held in Memphis, May 1927, and at the O.S.A. held in Schenectady, N.Y., October 1927. For abstract, see Jour. Opt. Soc. Am., and Rev. Sci. Inst., 16, p. 116, February 1928. The symbol N'' was used because the symbol N' had already been used in the derivation.

[9] The author was at that time employed at the Bureau of Standards as a Research Associate representing the A.O.C.S.

III. TESTED GLASSES

The 1,000 glasses, to which regrade numerals, N'', have been assigned range in nominal grades, N, from 0.09 to 20.0 Lovibond units. All engravings on each glass as received at the Bureau have been recorded, because of interest and possible service in establishing the origin, age, and history of the individual glass. Facsimiles of the various types of engravings are on file. For the same reasons, the thickness [10] of the center in millimeters, the character of the edges, and the surface imperfections in the middle third of the area have been carefully noted and are on record. For precision work, it would be desirable to have standards whose surfaces are plane and parallel, and which are free from pits, scratches, striae, bubbles, and haze. Very few of the glasses tested could be considered as ideal standards in these respects, yet none have been recommended for rejection. Some of the defects noted are in all probability the result of usage.

During the period when regrading was being done in cooperation with the A.O.C.S., the glasses were submitted with "AOCS numbers" engraved by A. W. Putland, who kept the key to these numbers, this being the only means of identification. Since then, Bureau of Standards test and serial numbers have served as a means of identification.

IV. APPARATUS

The apparatus (fig. 1) consists essentially of a Martens photometer [11] with auxiliary parts providing both a support for the glasses and a source of illumination.[12] The main parts are: Lamp inclosure, Davis-Gibson liquid filter, biprism and lens system, black chamber, Martens photometer, and eyeshield.

The field of view in the photometer is a 6-degree circular field divided along its vertical diameter. Each half of the circular field is illuminated by light diffusely reflected from an inclosure lined with magnesium oxide on white porcelain enamel and containing two 100-watt gas-filled tungsten lamps. The light reflected from the center of the rear surface of the inclosure passes through a window opposite the rear surface. The color temperature of the reflected light is maintained approximately at 2,848 K by means of a rheostat and voltmeter.

Before entering the photometer, the light passes through a Davis-Gibson filter [13] which gives it a spectral energy distribution approximating that of noon sunlight (Abbot-Priest sun). The filter consists of two solutions [14] encased in a double glass cell, the principal constituent being a blue solution which approximately converts the yellowish incandescent light to sunlight. By means of lenses and a biprism the artificial sunlight is directed through the black chamber into the photometer to give a uniform photometric field. The black chamber

[10] There is no correlation between thickness and grade, because the glasses are flashed. The average size of a Lovibond glass is approximately 50 by 17 by 2.5 mm.

[11] For original technical description, see Phys. Zeitschrift, 1, pp. 299–303, 1900.

[12] The original source of illumination was that of natural north skylight transmitted through milk glass. However, the grading of glasses was greatly delayed because the illumination was frequently insufficient. The present equipment, using artificial sunlight, provides a constant illumination and furthermore yields a much higher brightness than that previously obtained. A few glasses graded with the skylight illumination were regraded with the new equipment with entirely consistent results.

[13] R. Davis and K. S. Gibson, Filters for the Reproduction of Sunlight and Daylight and the Determination of Color Temperature, B.S.Misc.Pub. 114, January 21, 1931, p. 157.

[14] The filter and lamps were in use during the period of a year, from April 1928 to April 1929, the lamps being burned for about 700 hours. At the end of this time both the spectral transmission of the filter and the color temperature of the light source were determined. Results indicated that the lamps had become slightly yellower and the filter slightly bluer, so that, for our purpose, the total effect was negligible. It should be noted that little change in the grade assigned to a glass is to be expected, even with a considerable change in the relative energy distribution of the illuminant, because the glass tested and the combination of standards matching it had nearly the same spectral transmissions.

contains three slots, each slot of sufficient size to hold two glasses, one in each beam. The central portion of each glass, when in position in the black chamber, is effective in transmitting light to the photometer field.

By a rotation of the dial attached to the nicol prism, the two halves of the photometric field can be made equal in brightness. Attached

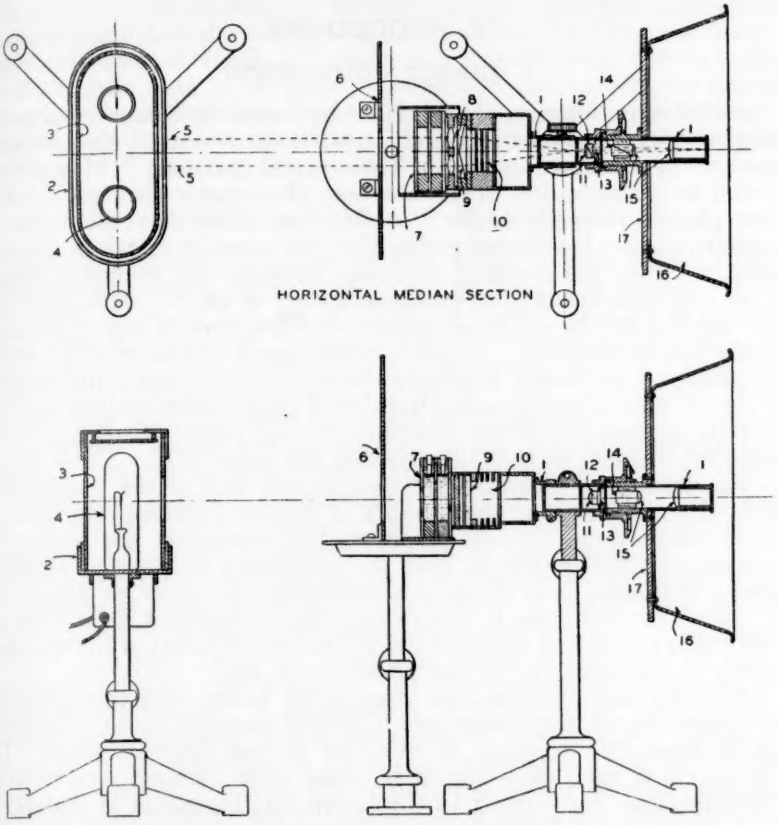

FIGURE 1.—*Apparatus used in the routine grading of Lovibond red glasses.*
In the vertical median section the supports are shown in outline rather than in section.

1. Martens photometer
2. Lamp inclosure
3. Magnesium oxide on white enamel
4. 100-watt gas-filled tungsten lamp
5. Rays from light source
6. Light shield
7. Davis-Gibson liquid filter
8. Lens
9. Biprism
10. Black chamber for holding Lovibond glasses
11. Objective lens of Martens photometer
12. Wollaston prism
13. Biprism of Martens photometer
14. Analyzing nicol prism
15. Ramsden ocular
16. Eyeshield
17. Knurled edge

to this dial is a pan-shaped eyeshield, painted black, with a knurled edge, the circumference of which is about 63 cm. This eyeshield serves two purposes: (1) The unused eye may remain open during observations; (2) due to the large lever arm of the knurled edge, fine adjustments of the nicol prism are possible.

A few other details of the apparatus may also be mentioned. A metal holder (not shown in fig. 1) for the 35Y glass fits over the

ocular of the Martens photometer and is attached by set screws to the tube containing the lens for bringing the divided circular field into focus. A metal shield between the lamp enclosure and liquid filter prevents glare from the light source when the observer interchanges glasses. The various parts of the apparatus are all mounted on the same base and adjustments for height are possible.

V. PROCEDURE

1. DIRECT COMPARISON

As stated previously, the glass to be tested is compared directly under artificial sunlight illumination with the standard glass or combination of standard glasses. The central portions [15] of each are viewed in juxtaposition in the Martens photometer through the 35Y glass placed over the ocular. A standard glass or combination of standard glasses is selected giving the best possible match in chromaticity.[16] Since the smallest intervals between the standard glasses in use are differences of approximately 0.1 of an N'' unit, estimates between the tenths are made whenever differences of this small magnitude can be detected. When a combination of two or more standard glasses is necessary to secure the match, the glass being tested is combined with a corresponding number of clear glasses, so that the light illuminating one half of the photometric field passes through as many reflecting surfaces as that illuminating the other half. Three glasses are the maximum number ever used in one half of the photometric field. By thus limiting the number of standard glasses errors due to the accumulation of small errors in the standards are prevented. Because of this limitation, and the restricted number of standard glasses available, it is frequently necessary, in order to obtain the N'' value for the glass tested to combine a standard glass with the glass being tested and subtract its N'' value from that of the standard glasses in the other half of the photometric field.

After the first decision, the glass being tested and the standards are interchanged in position and a second decision made. An average of these two readings is recorded as one determination. The final grade of each glass tested is based upon at least two separate determinations embodying two different combinations of standards. To increase the reliability of the average grade, a third or fourth combination of standard glasses is occasionally used, especially when the glass tested is of nominal grade greater than 10.0 Lovibond units.

Decisions are made near the position of brightness match. Ease of observation resulting in a very rapid and precise decision regarding a chromaticity match is attained by keeping the fixation on the brighter half of the field close to the dividing line, while the nicol prism is rotated rapidly back and forth in a small angle through the position of brightness match.[17]

---

[15] Lovibond numerals, N, are based on measurements made through the ends of the glasses opposite the engraved numerals.

[16] "The term *chromaticity* may be used to characterize a color qualitatively without reference to its brilliance. Chromaticity is determined by hue and saturation together, a gray being specified by the statement that it has no chromaticity." Report of the Colorimetry Committee, Optical Society of America, Jour. Opt. Soc. Am. and Rev. Sci. Inst., 6, p. 535, August 1922.

[17] Some observers prefer to make their decisions keeping their fixation on the darker half of the field while the nicol prism is rotated through the position of brightness match. However, the decisions on these 1,000 glasses were made in the former way. This factor as an aid to detection of chromaticity differences has been mentioned in a paper by D. B. Judd, Precision of Color Temperature Measurements under Various Observing Conditions; A New Color Comparator for Incandescent Lamps, B.S. Scientific Paper 252, 5, p. 1163, 1930.

2. CROSS-CHECKING

The regrade numerals, N'', obtained by the above procedure are subject to errors from a variety of sources, viz, (1) errors in N'' assigned to the standard glasses, (2) uncertainty of observation, and (3) errors of recording. To detect important errors in the values of N'' obtained for the glasses tested, each of these glasses is compared with its successive neighbor in the same group. This intercomparison or cross-check has the decided advantage that, for the most part, a single standard of small N'' value is required, with corresponding small absolute error in its value. Consistent results between regrade and cross-check data are obtained before any regrade numerals are certified, although the cross-check data do not enter into the computations of the regrade numerals.

3. CERTIFICATION AND RELIABILITY

Regrade numerals, N'', are certified to be correct within certain tolerances depending upon the nominal grades of the glasses. These tolerances are (*a*) 0.1 of an N'' unit for glasses ranging in nominal grade from the smallest value submitted up to and including 10.0; (*b*) 0.2 of an N'' unit for nominal grades greater than 10.0 and those up to and including 16.0; (*c*) 0.4 of an N'' unit for nominal grades greater than 16.0 and those up to and including 20.0. Theoretically, the tolerances should not be assigned in this step-like fashion, since previous tests have shown that the red-difference just perceptible with certainty increases continuously as N'' is increased. Nevertheless, it has seemed unnecessary and impracticable to attempt any finer gradation of the tolerances than those just given.

These tolerances were based upon the writer's chromaticity discrimination at various points on the scale of 35 yellow plus N'' red (35Y+N''R). A determination of this sort was made in August 1927 at 35Y plus 7.6R (an important point on the scale in the oil industry) [18] before the duties of routine testing of Lovibond red glasses were assigned. A difference of 0.16 [19] of an N'' unit was perceptible with certainty and a difference of 0.093 of an N'' unit was named correctly eight out of ten times. A few months later, a difference of N'' equal to 0.10 at 35Y+7.6R was perceived with certainty. The following table shows the approximate minimum differences perceptible [20] with certainty by the writer near the points indicated on the 35Y+N''R scale:

Point on scale (35Y+N'' R)	N''=7.6	10.0	17.1	19.7
Minimum difference in N'' perceptible with certainty	=0.10	.10	.20	.30

It is seen that these differences do not exceed the tolerances; that is, in no case would a difference as large as the tolerance go undetected even in a single observation.

[18] "Prime Summer Yellow Cotton Seed Oil must be * * * of no deeper color than the two combined standard glasses of 35 yellow and 7.6 red on Lovibond's equivalent color scale * * *" Rule 61 of the rules governing transactions between members of the National Cottonseed Products Association, Inc. It is interesting to note that the occasion for the introduction of Lovibond glasses into the United States, which occurred about 1900, was the establishment of this standard of color for Prime Summer Yellow Cotton Seed Oil.

[19] Tests of Color Sense of A.O.C.S. Members and Data on Sensibility to Change in Lovibond Red, by I. G. Priest, Oil and Fat Industries, 5, pp. 66–67, March 1928.

[20] An analysis of extensive data on 36 Lovibond red glasses submitted for test in terms of our standard glasses, showed that the precision and reproducibility to be expected from this chromaticity discrimination were being realized (D. B. Judd, Chromaticity Sensibility to Stimulus Differences, Jour. Opt. Soc. Am., 22, p. 98, February 1932). It also showed that the routine procedure involves enough determinations to keep the error well within the tolerances.

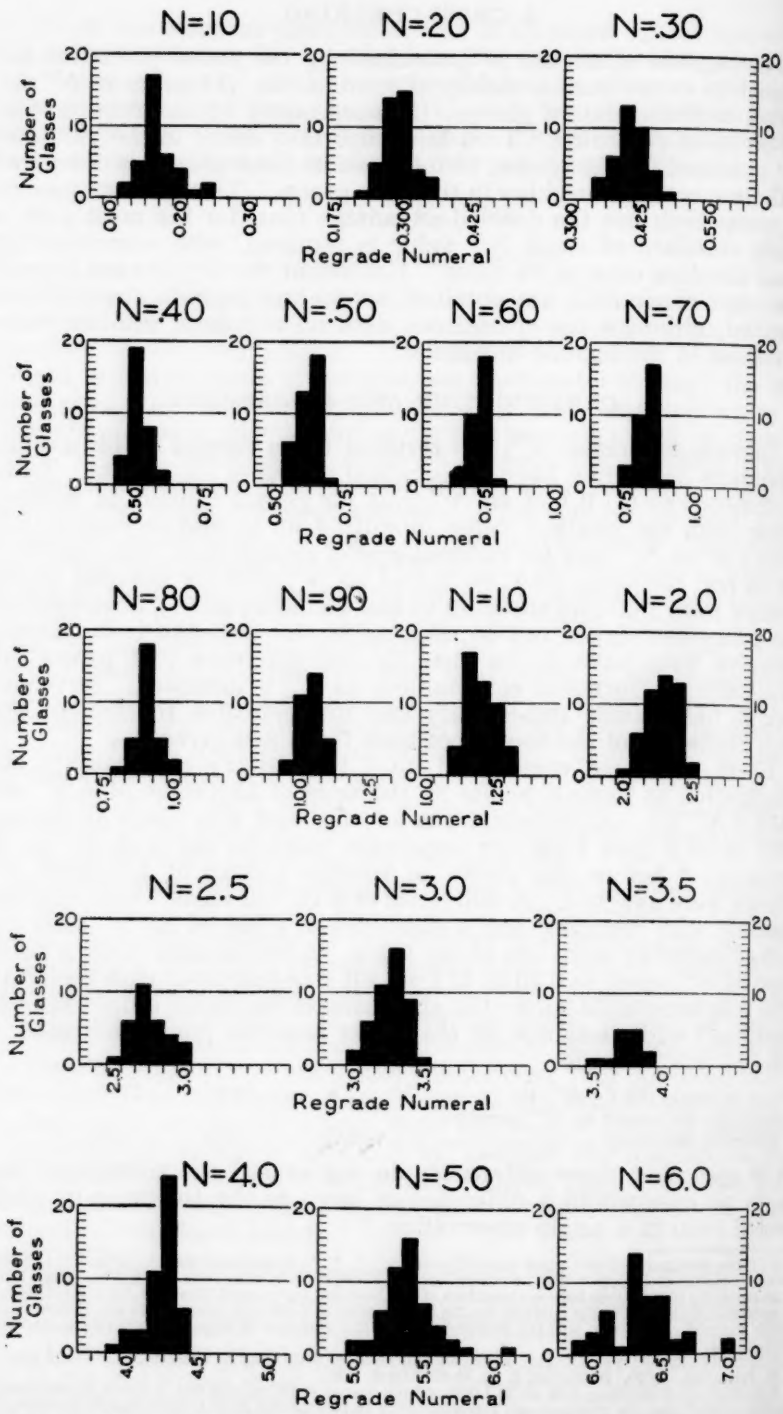

FIGURE 2.—*Frequency distributions of regrade numerals.*

The reliability of the regrade numerals is further emphasized from the evidence of uniformity obtained in the intercomparison or cross-checking of the glasses tested.

VI. DISCUSSION OF RESULTS

1. VARIATIONS AMONG GLASSES OF IDENTICAL NOMINAL GRADE

The results of this phase of the statistical investigation are presented both in graphical and tabular form. The variations in the

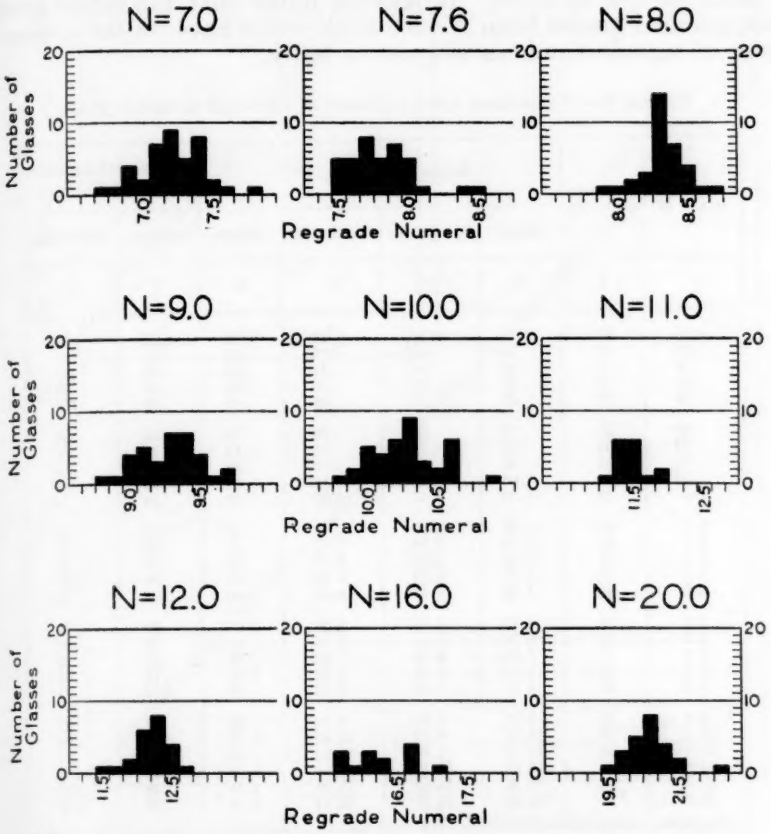

FIGURE 3.—*Frequency distributions of regrade numerals (continued).*

Figures 2 and 3 show the distributions of regrade numerals, according to the Priest-Gibson (N'') scale, for each group of Lovibond red glasses having nominal grade, N. The ordinate indicates the number of glasses having the regrade numeral shown on the abscissa. Each group is composed of glasses having identical maker's numerals engraved upon them, and no group shown contains fewer than 14 glasses. The regrade numerals, N'', are certified to be correct within certain tolerances depending upon the nominal grades of the glasses. The following table shows the tolerances which have been assigned to the ranges of nominal grades indicated:

Range	Tolerance
$0.01 \leq N \leq 10.0$	$N''=0.1$
$10.0 < N \leq 16.0$	$N''= .2$
$16.0 < N \leq 20.0$	$N''= .4$

regrade numerals, N'', occurring within the larger groups of glasses (912 glasses in all) of identical grade, N, are illustrated in figures 2 and 3. These column diagrams represent the frequency distributions of the regrade numerals for glasses of identical nominal grade.

The means of the regrade numerals of glasses composing each group are given in table 2, column 3, and are plotted as circles in figure 4, the vertical lines indicating the ranges between the minimum and maximum values of the regrade numerals in each group. These minimum and maximum values and the ranges of the regrade numerals are also given in table 2, columns 4, 5, and 6. The ranges of the regrade numerals vary from 0.12 to 3.23 N'' units, depending upon the nominal grades of the groups; in every case these ranges of N'' exceed the tolerances specified in section V, 3, in many cases by a factor of five or more. It may be noted that the larger groups with nominal grades from $N=5.0$ to $N=12.0$ have on the average a range of regrade numerals as great as unity.

TABLE 2.—*Variations among glasses of identical nominal grade*

Nominal Grade N	Number of glasses	Regrade numerals, N''				Deviations from mean in column 3	
		Mean	Minimum	Maximum	Range	Average	Maximum
1	2	3	4	5	6	7	8
0.10	37	0.16	0.11	0.24	0.13	0.02	0.08
.20	42	.29	.22	.36	.14	.02	.07
.30	37	.41	.34	.47	.13	.02	.07
.40	33	.51	.45	.59	.14	.03	.08
.50	38	.62	.55	.68	.13	.03	.07
.60	31	.73	.66	.78	.12	.02	.07
.70	31	.83	.76	.88	.12	.03	.07
.80	31	.90	.82	1.00	.18	.03	.10
.90	32	1.04	.96	1.12	.16	.03	.08
1.0	48	1.20	1.11	1.30	.19	.04	.10
2.0	48	2.27	2.02	2.47	.45	.09	.25
2.5	31	2.74	2.54	2.97	.43	.09	.22
3.0	45	3.25	2.97	3.47	.50	.10	.28
3.5	14	3.73	3.51	3.89	.38	.08	.22
4.0	48	4.25	3.93	4.43	.50	.08	.32
5.0	53	5.38	4.99	6.07	1.08	.14	.69
6.0	49	6.36	5.93	6.98	1.05	.18	.62
7.0	41	7.21	6.74	7.83	1.09	.17	.62
7.6	38	7.80	7.46	8.52	1.06	.18	.72
8.0	34	8.32	7.91	8.70	.79	.12	.41
9.0	35	9.27	8.80	9.70	.90	.17	.47
10.0	39	10.27	9.77	10.90	1.13	.19	.63
11.0	16	11.47	11.10	11.92	.82	.18	.45
12.0	23	12.22	11.53	12.61	1.08	.20	.69
16.0	14	16.26	15.61	17.06	1.45	.38	.80
20.0	24	20.69	19.51	22.74	3.23	.50	2.05

As a further indication of the variations or dispersions of glasses of identical grades, the mean and maximum deviations from the mean regrade numerals are given in table 2, columns 7 and 8. Approximately 25 percent of the total number of glasses have regrade numerals which differ from the respective means of the groups by more than our tolerances.

Not only is the range within any group large, but in most cases an overlapping of regrade numerals exists in two adjacent groups (fig. 4). In some instances, especially among the larger groups from $N=5.0$ to $N=12.0$, glasses of similar chromaticity have nominal grades differing by a nominal unit.

2. FAILURE OF ADDITIVITY IN THE LOVIBOND RED SCALE WHEN COMBINED WITH 35Y

Because of the size of the variations just shown among glasses of the same nominal grade, it is not surprising that the glasses in any

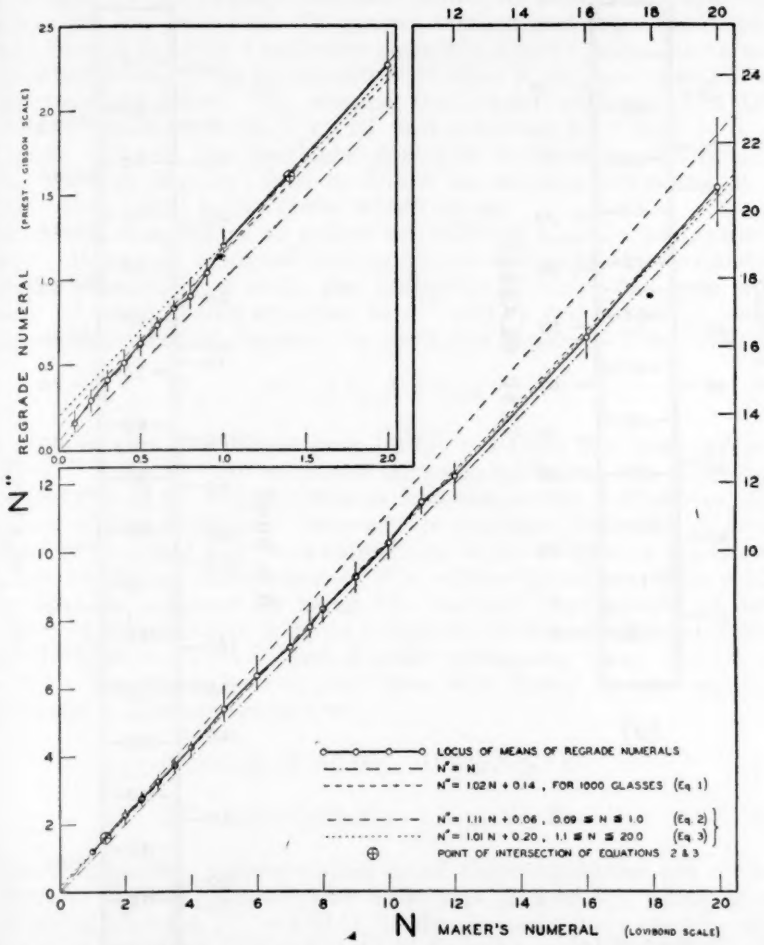
N'' REGRADE NUMERAL (PRIEST - GIBSON SCALE)
N MAKER'S NUMERAL (LOVIBOND SCALE)
LOCUS OF MEANS OF REGRADE NUMERALS
N''= N
N''= 1.02 N + 0.14 , FOR 1000 GLASSES (Eq 1)
N''= 1.11 N + 0.06 , 0.09 ≤ N ≤ 1.0 (Eq 2)
N''= 1.01 N + 0.20 , 1.1 ≤ N ≤ 20.0 (Eq 3)
POINT OF INTERSECTION OF EQUATIONS 2 & 3

FIGURE 4.—*Graphical summary of results showing the variations among glasses of the same nominal grade (N) and the nature of the disagreement between the N'' and N scales using data on the glasses graded.*

The inset shows the data for N less than 2.0. The vertical lines indicate the ranges between the minimum and maximum values of the regrade numerals in each group. It is seen that the plotted points representing the average N'' values of the groups do not fall along the line $N''=N$. No simple adjustment can bring the N'' and N scales into agreement for the general disagreement is complex, being both erratic as well as regular in nature. The latter permits the data to be satisfactorily represented by two straight lines (equations 2 and 3), one for low and one for high values of N. However, it may be seen that the variations of regrade numerals (N'') among glasses of the same nominal grade (N) constitute the major source of error.

one set fail to satisfy the additivity condition. This failure of additivity, due to the erratic variations in the size of intervals between successive Lovibond tenth and unit glasses, is well illustrated by a series of 29 glasses selected from the Bureau's set, B.S. 9940, which

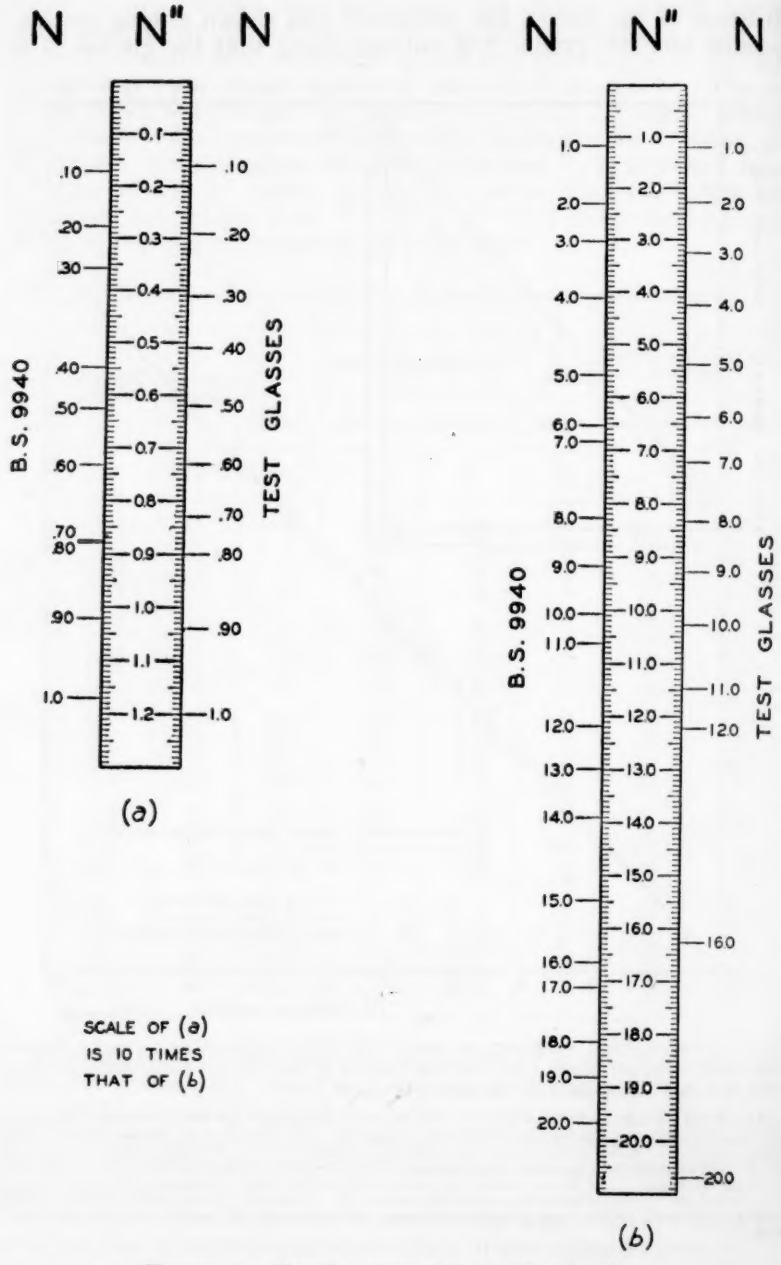

FIGURE 5.—*Erratic nature of the Lovibond scale.*

The variations occurring among glasses of an individual set, B.S. 9940, may be compared with the average variations found among the glasses sent in for calibration.

range in N from 0.10 to 1.0 in multiples of 0.1 (tenth glasses) and from 1.0 to 20.0 in multiples of 1.0 (unit glasses). Figure 5 shows these nonuniform N intervals in terms of the standard scale, N''.

It might be expected that if sufficient glasses of each nominal grade were calibrated, the erratic variations in their intervals would average out, so that on the average the scale would be additive. However, this was not the case with the glasses studied and reported herein, as may be seen in figure 4 and more clearly in figure 5, where the mean regrade numerals, given in column 3 of table 2, are also marked off on the standard scale. The nominal tenth intervals vary from 0.07 to 0.16 N'' units and the nominal unit intervals from 0.85 to 1.13 N'' units. Hence, this particular group of nominal tenth and unit glasses (829 in number) fails to follow an additive scale and it is unlikely that a still larger group would do so.

Moreover, this failure to follow an additive scale is not entirely erratic. It may be analyzed into regular as well as erratic deviations from the Priest-Gibson scale, the additivity of which has been confirmed. A straight-line equation in N'' and N was found by least-squares adjustment of the data for the 1,000 glasses. This equation is:

$$N''=1.02\ N+0.14 \tag{1}$$

The slope of this line differs from unity, but since any scale related to the N'' scale by any constant factor is additive, this deviation from unity is of no consequence in this connection. However, the existence of the significant intercept is evidence that the N scale deviates in a regular way from conformity to the additivity condition.

A more accurate description of this regular departure from additivity may be obtained by using two straight lines instead of one. The plotted points shown in figure 4 suggest one straight line extending from $N=0.09$ to $N=1.0$, and another extending from $N=1.1$ to $N=20.0$. Equations for two such lines were found by least-squares adjustment. The equations are:

$$N''=1.11\ N+0.06, \quad 0.09\leqq N\leqq 1.0 \tag{2}$$

$$N''=1.01\ N+0.20, \quad 1.1\ \leqq N\leqq 20.0 \tag{3}$$

The straight lines corresponding to all three equations are shown on figure 4. It will be noted that equations (2) and (3), which agree at the point ($N=1.4$, $N''=1.614$), fit the plotted values considerably better than equation (1); hence they describe more accurately the relation between the N and N'' scales. The intercepts are again evidence of a regular departure from additivity even for the lower section of the scale. Furthermore, the greater slope of equation (2) indicates that the size of the N unit is larger for the lower section of the scale ($N<1.4$) than for the upper ($N>1.4$). If the glasses of the lower section are used in combination with those of the upper, this disparity in the size of the N unit will in itself also introduce errors of nonadditivity. This is a second regular type of failure of the N scale to satisfy the additivity condition, and is distinct from that indicated by the intercepts.

A still more accurate description of the variations in the size of the N unit might possibly be accomplished by setting up equations of the second or higher degree. However, such refinement is not

required here, since the object has been to show the degree to which the Lovibond scale, embodied in these 1,000 red glasses combined with 35Y, fails to be additive. Both regular and erratic departures from additivity have been demonstrated. Of the two, the erratic departures are the more important; it has been shown that the discrepancies between glasses of the same nominal grade frequently amount to a whole unit.

WASHINGTON, October 13, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP654

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A METHOD FOR THE SEPARATION OF RUTHENIUM FROM PLATINUM, PALLADIUM, RHODIUM, AND IRIDIUM

By Raleigh Gilchrist

ABSTRACT

A procedure for the separation and gravimetric determination of ruthenium is described. The method of separation differs essentially from existing methods in that the ruthenium is distilled from a solution of its sulphate in diluted sulphuric acid containing sodium bromate. A very suitable reagent for the quantitative absorption of the distilled tetroxide was found to be diluted hydrochloric acid saturated with sulphur dioxide. The recovery of ruthenium is accomplished by precipitating the hydrated oxide from a boiling solution at pH6, after sulphite compounds have been decomposed by treatment with hydrochloric acid. The hydrated oxide is ignited in the air to an anhydrous oxide which is then reduced to metal under hydrogen.

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I. INTRODUCTION

In a previous paper [1] from this laboratory, a method was described for the quantitative precipitation of ruthenium as a hydrated oxide from chloride solution and for its determination as metal. The purpose of this paper is to present a method for the separation of ruthenium from the other platinum metals, and to combine this method with that mentioned above.

Ruthenium and osmium, through their ability to exist as volatile tetroxides, can be removed from solution by distillation. Advantage has been taken of this property in every scheme of analysis which has been proposed. Sufficient differences exist in the conditions affecting the formation of these two volatile compounds so that they can be separated from each other, or they can be distilled together from the same solution. The customary procedure has been first to distill a

[1] R. Gilchrist, B. S. Jour. Research, vol. 3, p. 993, 1929.

solution strongly acid with nitric acid, thereby eliminating osmium, and then to make the solution strongly alkaline, saturate it with chlorine, and distill again to remove ruthenium. In one method, at least, that of Leidié [2], the two tetroxides are distilled simultaneously from an alkaline hypochlorite solution and subsequently separated from each other.

In a recent study of the separation and determination of osmium,[3] it was found that no ruthenium was volatilised from solutions containing as much as 40 percent of nitric acid by volume. During the distillation of osmium from nitric-acid solution, the other platinum metals remain as soluble compounds in the distilling flask.

During the subsequent distillation of ruthenium from an alkaline hypochlorite solution, on the other hand, a precipitate consisting of the hydrated oxides of iridium, rhodium and palladium separates as the hot alkaline solution becomes saturated with chlorine. It has been repeatedly observed that such a precipitate carries with it some ruthenium. It then becomes necessary to cool the solution, to add fresh alkali, and to repeat the saturation with chlorine. Such treatment must be repeated a number of times without certainty of complete removal of the ruthenium. A procedure of this kind becomes extremely tedious and furthermore causes the introduction of a great quantity of alkali salts which interfere with subsequent analytical operations. From a solution containing 0.1670 g of ruthenium in the presence of 1.4 g of iridium, only 0.1623 g of ruthenium was recovered, although the treatment with additional alkali and the saturation with chlorine was repeated six times and no more ruthenium appeared to distill. This result confirms previous observations on the incomplete elimination of ruthenium by this method in refining operations. On the contrary, in three experiments in which 0.1901 g, 0.1658 g, and 0.1468 g of ruthenium were taken and iridium was absent, 0.1900 g, 0.1659 g, and 0.1468 g of ruthenium were recovered, respectively. Distillation was continued for 1½ hours after saturating the cold solutions with chlorine, although the ruthenium appeared to be practically all removed in the first 15 minutes after boiling began. Since iridium invariably accompanies ruthenium in platiniferous materials, there appears to be little hope that this method can be made the basis of a simple, accurate means for isolating ruthenium analytically.

In the experiments just mentioned, the ruthenium tetroxide was caught in diluted hydrochloric acid (1+1) [4] contained in four flasks, the last one with a little alcohol also. The ruthenium was distributed throughout the four flasks, but only a small amount was present in the last one.

Another method of separating ruthenium, which was proposed only a few years ago in a scheme of qualitative analysis, consists in distilling ruthenium tetroxide from perchloric acid.[5] Attempts to use this procedure were made in this laboratory [6] but it was found

[2] E. Leidié, Compt. rend., vol. 131, p. 888, 1900.
[3] Gilchrist, B. S. Jour. Research, vol. 6, p. 421, 1931.
[4] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; sulphuric acid, the concentrated acid of specific gravity 1.84; nitric acid, the concentrated acid of specific gravity 1.42; and hydrobromic acid, the 40 percent acid of commerce. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.
[5] A. A. Noyes and W. C. Bray, Qualitative Analysis for the Rare Elements. The MacMillan Co., 1927.
[6] Unpublished work by H. A. Buchheit.

that here again iridium dioxide precipitated in the distilling flask when the solution was heated until vapors of perchloric acid were evolved and that the separation of ruthenium was not complete.

H. E. Holbrook,[7] of the H. A. Wilson Co., suggested a method in which precipitation of iridium dioxide is avoided by distilling from a solution containing sulphuric acid. In this method, the product formed in an alkali-nitrate fusion of the ruthenium material is treated with water containing sulphuric acid and placed in a distilling apparatus together with sodium chlorate and sodium chloride. The resulting solution is heated to boiling and the ruthenium eliminated as the tetroxide. In attempting to use this method for distilling ruthenium tetroxide from a solution of ammonium chlororuthenate in diluted sulphuric acid, a deposit of ruthenium dioxide was frequently obtained on the inner walls of the distilling flask and of the delivery tube leading to the first absorbing flask. The cause of this unexpected behavior did not become apparent until somewhat later when it was finally traced to the presence of hydrochloric acid which reduced the hot tetroxide vapors.

Further attempts to use sodium chlorate as an oxidizing reagent were abandoned, when, in the meantime, it was found that sodium bromate was a much more suitable reagent.

II. DISTILLATION OF RUTHENIUM FROM ACID SOLUTIONS CONTAINING SODIUM BROMATE

It was observed that ruthenium tetroxide is produced when a neutral or acid solution containing ruthenium is treated with sodium bromate or with sodium chlorate. In acid solution, the bromate ion and the chlorate ion are comparatively stable toward sulphuric acid or nitric acid but are readily decomposed by either hydrochloric or hydrobromic acid.

The problem at hand was to establish conditions suitable for the rapid and complete elimination of ruthenium and to prevent the precipitation of the other platinum metals during the operation. A number of preliminary experiments were made in which such factors as the following were varied: The nature and quantity of the acid added to prevent precipitation in the distilling flask; the nature and quantity of the reagent solution added to oxidize the ruthenium to the tetroxide; the temperature at which the distillation should be conducted; the preparation of the ruthenium solution previous to distillation; the length of time of distillation; the effect of the presence of other platinum metals.

The apparatus used was the same as that described in a previous paper [8] and which is shown in figure 1 in the section on recommended procedure. The solution used to absorb the liberated tetroxide consisted of diluted hydrochloric acid (1 + 1), freshly saturated with sulphur dioxide. The initial volume of the ruthenium solution in the distilling flask was 100 ml in each instance. The volume of the solution at the end of the distilling operation was usually between 200 and 300 ml, owing to the addition of the oxidizing reagent and of water necessary to keep the liquid column in the thistle tube free from dissolved tetroxide.

It was found that sulphuric acid was the most suitable of the commonly available acids for use in the distilling flask and that 10 ml of

[7] Private communication.
[8] See footnote 3, p. 284.

it was sufficient, in the volume used, to prevent the precipitation of iridium dioxide. Hydrochloric acid and hydrobromic acid were not only unsuitable but objectionable. When present in even small quantities, they caused decomposition of the bromate ion and the evolution of large amounts of bromine. Furthermore, their presence caused a film of ruthenium dioxide to be formed on the walls of the apparatus unless care was taken to control the temperature of distillation. No way was found by which this film could be readily dissolved and as a consequence its formation had to be avoided.

It was found possible to distill ruthenium from a nitric-acid solution so that this operation could be conducted immediately after the elimination of osmium by simply adding sodium bromate. In analysis no. 516 (table 1), the ruthenium was distilled from diluted nitric acid (1 + 9) to which it was found necessary to add 5 ml of nitric acid as

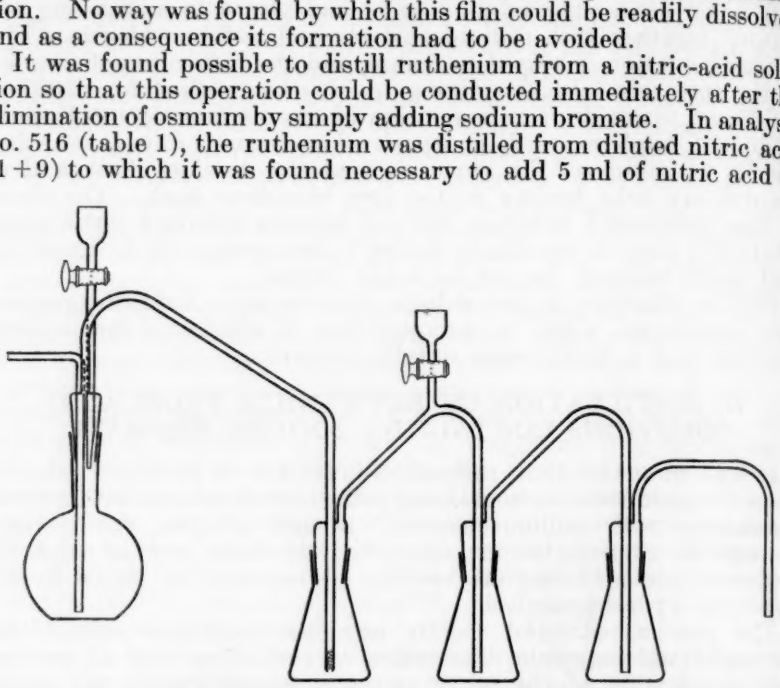

FIGURE 1.—*Distilling flask with train.*

the distillation progressed, in order to prevent hydrolytic precipitation of the iridium. While this procedure can be used, it has the disadvantage that distillation of nitric acid causes a rather large quantity of sulphuric acid to be formed by reaction in the absorbing solution, the presence of which was found to interfere in the hydrolytic precipitation of hydrated ruthenium oxide unless the evaporated absorbent solution was first heated until vapors of sulphuric acid [9] were evolved.

No advantage appeared to be gained by adding the bromate either continuously or at intervals, nor did the addition of bromide appear to be useful or desirable. In analyses nos. 505 and 506, a mixed solution of sodium bromate and sodium bromide was added intermittently, while in analysis no. 507 this mixture was dripped in continuously. In all of the experiments which follow analysis no. 516 in numerical order, only bromate was used, the entire amount of which, 100 ml of a 10 percent solution, was added at the start of the distillation. In the other experiments reported in table 1, the bromate solution was added at intervals and varied in total amount from 40 to 100 ml.

[9] That no significant loss of ruthenium occurs when such a solution is heated until vapors of sulphuric acid are liberated is shown by the result obtained in analysis no. 516 as well as by those given in table 2, which confirm the observation reported in the paper on the separation of osmium. (See footnote 3, p. 284.)

It was observed that the nature of the ruthenium compound taken as the sample had some effect on the ease with which the tetroxide was formed. When taken as the chlororuthenate, as in analyses nos. 502 to 509, a considerable length of time was necessary to remove the last trace of ruthenium. In marked contrast to the relatively slow formation of tetroxide from the chlororuthenate was the rapid formation of ruthenium tetroxide from ruthenium sulphate. A further advantage that is gained by distilling from a solution of ruthenium which has been heated until vapors of sulphuric acid are formed is that hydrochloric acid and hydrobromic acid are absent, and consequently the entire distilling operation can be conducted at the boiling temperature without danger of the deposition of ruthenium dioxide. The minimum time required under these conditions was found to be 2 hours.

The presence of iridium, palladium, rhodium, and platinum in solutions which had not been evaporated with sulphuric acid was found to have no effect on the separation of ruthenium, provided a sufficient quantity of sulphuric acid, 10 ml, had been added. In solutions which had been heated until vapors of sulphuric acid were given off, ruthenium, iridium, rhodium, and palladium formed soluble sulphates, while most of the platinum separated as metal. The metallic platinum thus precipitated, however, was found not to affect the elimination of ruthenium.

The results of the preliminary experiments are given in table 1. The amount of ruthenium in the residual solutions was determined colorimetrically by comparison with solutions of known ruthenium content. For this purpose, the solutions were first saturated with sulphur dioxide and treated with a few crystals of thiourea. On standing for 24 hours, a greenish or bluish color developed, depending upon the amount of ruthenium present.

TABLE 1.—*Results of the preliminary experiments on the distillation of ruthenium tetroxide*

Analysis no.	Ruthenium salt taken	Ruthenium present [1]	Ruthenium recovered	Error	Test for ruthenium in residual solution	Total time of distillation	Other platinum metals present	Remarks
	g	*g*	*g*	*g*		*hr*	*g*	
502	0.4772	0.1415	0.1415	0.0000	Less than 0.1 mg	9		
503	.4410	.1308	.1310	+.0002	Colorless	4		
505	.4727	.1402	.1398	−.0004	Approximate 0.5 mg.	3½		Stopped at end of 3½ hr.
506	.4216	.1250	.1237	−.0013	Slightly greater than 1 mg.	4		Stopped at end of 4 hr.
507	.3977	.1180	.1180	.0000	Less than 0.1 mg	7		
511	.3513	.1042	.1043	+.0001	Colorless	4		
512	.3524	.1045	.1044	−.0001	0.1 mg	3		
516	.4166	.1236	.1237	+.0001	Colorless	3½		Distilled from nitric acid.
520	.3689	.1094	.1093	−.0001	0.1 mg	10		No Ru appeared to distill after 3½ hr.
509	.3676	.1090	.1091	+.0001	Not made	11½	0.093 Ir	No Ru appeared to distill after 5 hr.
510	.4109	.1219	.1222	+.0003	do	5½	.015 Ir .020 Rh .010 Pd .050 Pt	
621-601	.5274	.1564	.1565	+.0001	do	7	.1426 Ir	Distilled 3½ hr at 70 C, 3½ hr at boiling temperature.
623-602	.5247	.1556	.1556	.0000	do	7	.1605 Ir	Distilled 4 hr at 70 C, 3 hr at boiling temperature.

[1] Calculated on the basis of an experimentally determined ruthenium content of 29.66 percent.

NOTE.—In analyses nos. 621-601 and 623-602, the iridium which had been added was recovered by hydrolytic precipitation at pH 6 and determined as metal. The quantities of iridium recovered were 0.1427 g and 0.1603 g, respectively. The slight loss in the recovery in analysis no. 623-602 was caused by a faint mirror of iridium dioxide which could not be removed from the beaker in which the precipitation was made.

The results of the experiments in which ruthenium was distilled from solutions which had first been heated until copious vapors of sulphuric acid were evolved, according to the procedure finally adopted, are given in table 2. In these experiments, 100 ml of a 10 percent solution of sodium bromate was added to the solution in the distilling flask, the initial volume of which was 100 ml. In analyses nos. 625 and 626, the solutions were heated to boiling for 1 hour after most of the ruthenium had been eliminated at a somewhat lower temperature. This period of boiling proved to be insufficient and was increased to 1½ hours in analyses nos. 627, 628, and 629. It was later found that if the entire distillation was made at the boiling temperature a period of 2 hours is necessary and sufficient.

TABLE 2.—*Results of the determination of ruthenium when distilled from sulphate solution*

Analysis no.	Ruthenium salt taken	Ruthenium present[1]	Ruthenium recovered	Error	Test for ruthenium in residual solution	Total time of distillation	Other platinum metals present	Remarks
	g	*g*	*g*	*g*		*hr*	*g*	
625	0.4875	0.1446	0.1445	−0.0001	Less than 0.1 mg	2½		Distilled at boiling temperature for 1 hr.
626	.4412	.1309	.1307	−.0002	0.2–0.3 mg	3		Do.
627	.3844	.1140	.1140	.0000	Colorless	3½		Distilled at boiling temperature for 1½ hr.
628	.4192	.1243	.1244	+.0001	Not made	3½	0.2125 Ir	Do.
629	.3889	.1153	.1152	−.0001	do	3	.1955 Ir .0076 Rh .1084 Pd .2739 Pt	Do.

[1] Calculated on the basis of an experimentally determined ruthenium content of 29.66 percent.

III. METHOD OF ANALYSIS RECOMMENDED

The following procedure is designed to separate ruthenium as the volatile tetroxide from a solution containing the platinum group of metals, with the exception of osmium which must be absent; to recover the evolved tetroxide by absorption in diluted hydrochloric acid (1+1) which has been freshly saturated with sulphur dioxide; to precipitate the ruthenium as a hydrated oxide from the absorbent solution; and to obtain the ruthenium as metal.

1. DISTILLING APPARATUS

The distilling apparatus is shown in figure 1. It consists of three main parts, namely, a 700 ml distilling flask, a set of three 300 ml absorbing flasks, and a train of inlet and delivery tubes which are sealed into one piece. The thistle tube closed by a stopcock, placed between the first and second absorbing flasks, serves to replenish the absorbing solution with sulphurous acid and also to rinse the tube connecting the two flasks at the end of the distillation. The entire apparatus is constructed of pyrex glass. The joints must be very carefully ground, since no organic lubricant can be used except on the stopcock of the thistle tube which leads into the distilling flask. The joints are therefore sealed with a film of water only. The stem of the thistle tube which leads into the distilling flask should have a diameter which will allow a column of water to be held in it. It is extremely important that this tube be flushed occasionally in order to remove any tetroxide which diffuses into it.

2. PREPARATION OF THE SOLUTION

Evaporate to dryness on the steam bath the solution which remains in the distilling flask after the elimination of osmium. Add 5 to 10 ml of hydrochloric acid and again evaporate the solution. Repeat the evaporation with hydrochloric acid until oxides of nitrogen are no longer evolved. This precaution is taken to avoid the danger of a slight loss of ruthenium if the nitric-acid solution were simply evaporated and heated until vapors of sulphuric acid were formed. Dilute the chloride solution, add 10 ml of sulphuric acid, and evaporate carefully until heavy vapors of sulphuric acid are evolved. Transfer the solution and any metallic platinum which may have separated to the distilling flask and dilute it to about 100 ml with water.

3. SEPARATION OF RUTHENIUM

Place 150 ml of diluted hydrochloric acid (1+1), freshly saturated with sulphur dioxide, in the first receiving flask and 50 ml of the same solution in each of the other two receiving flasks. Add 100 ml of a 10 percent solution of sodium bromate through the thistle tube to the distilling flask. Pass a gentle current of air through the apparatus and heat the solution in the distilling flask to boiling. Distill at this temperature for 2 hours. Add a portion of freshly prepared sulphurous acid through the other thistle tube occasionally in order to replenish the absorbing solution with sulphur dioxide. At the end of the distillation, flush the delivery tube between the first and second absorbing flasks with sulphurous acid.

4. RECOVERY AND DETERMINATION OF RUTHENIUM

Combine the portions of the absorbing solution and evaporate to a moist residue on the steam bath. Add 10 ml of hydrochloric acid and digest the solution for ½ hour. Add 50 ml of water and heat the solution to boiling in order to complete the dissolving of the somewhat difficultly soluble ruthenium compound. When the ruthenium compound is completely dissolved, filter the solution and wash the filter with diluted hydrochloric acid (1+99). The solution is filtered to insure the elimination of a small amount of silica which may be present. Dilute the ruthenium solution to 200 ml, heat it to boiling, and add a filtered 10 percent solution of sodium bicarbonate until a precipitate begins to form. Add the bicarbonate solution dropwise until the acidity of the solution reaches a value of pH 6 as indicated by the change in color from yellow to blue of brom cresol purple indicator present in the solution. Boil the solution for 5 to 6 minutes and filter it.

Wipe the inner walls of the beaker and also the glass rod with a small piece of ashless filter paper. Thoroughly wash the filter and precipitate with a hot 1 percent solution of ammonium sulphate. Finally wash them 3 or 4 times with a cold 2.5 percent solution of ammonium sulphate.

Place the filter and precipitate in a porcelain crucible, dry them, and char the filter slowly. The dried filter will usually char completely when once it begins to smoke. This operation should be done carefully in order to prevent loss of ruthenium by deflagration. Ignite the residue strongly in air and then in hydrogen. Cool the

resulting metal in hydrogen and leach it well with hot water. This is done to insure complete removal of soluble salts. It is well to leach the residue in the crucible first and then to transfer it to a filter. Ignite the filter and metal in air and in hydrogen. Cool the residue in hydrogen and weigh it as metallic ruthenium.

The method which has just been given for the separation and determination of ruthenium is designed to follow the procedure for the separation of osmium in a general scheme for the analysis of the platinum group. The treatment of the solution which remains in the distilling flask after the separation of ruthenium will be given in a separate paper.

The writer wishes to express his appreciation of the helpful suggestions of Edward Wichers.

WASHINGTON, December 14, 1933.

U.S. Department of Commerce, Bureau of Standards

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METHODS FOR THE SEPARATION OF PLATINUM, PALLADIUM, RHODIUM, AND IRIDIUM FROM ONE ANOTHER AND FOR THEIR GRAVIMETRIC DETERMINATION

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ABSTRACT

A method is described for the analytical separation of platinum from each or all of the three metals, palladium, rhodium, and iridium. It is based upon the complete precipitation of the hydrated dioxides of palladium, rhodium, and iridium in a boiling solution containing sodium bromate and having an acidity of pH 6. Two precipitations of the hydrated dioxides were found to be sufficient to effect the quantitative isolation of platinum.

The separation of palladium from rhodium and iridium, by means of dimethylglyoxime, and its subsequent determination are also described. The procedure for the separation of rhodium from iridium by titanous chloride and for the determination of these two metals, given in detail in a previous publication from this laboratory, is discussed only briefly in this paper.

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I. INTRODUCTION

In a systematic scheme for the analysis of the platinum group, it is the usual procedure to remove osmium and ruthenium first as volatile tetroxides and then to effect the separation of the four remaining

platinum metals from one another. It has been the practically universal custom to effect these latter separations by means of potassium chloride or ammonium chloride. These reagents produce relatively insoluble compounds of the type K_2PtCl_6, $(NH_4)_2IrCl_6$, etc., with the quadrivalent platinum metal chlorides and soluble compounds with the ter- and bi-valent chlorides. In spite of the general use of potassium chloride or of ammonium chloride to effect the separation of iridium from rhodium, or of platinum from rhodium, or of platinum from iridium, these reagents can hardly be expected to produce clean-cut separations. Experience in this laboratory with the purification of the platinum metals has shown that rhodium contaminates iridium, when the latter is precipitated as ammonium chloroiridate, and that it can be completely eliminated only with great difficulty, if at all, by repeated precipitation of the iridium. Rhodium likewise contaminates platinum, when the latter is precipitated as ammonium chloroplatinate. Since the potassium and the ammonium salts of the quadrivalent platinum metal chlorides are slightly soluble, a small amount of iridium or of platinum must remain in solution, thereby contaminating the very metal from which complete separation is sought. This situation, unfortunately, is often disregarded. Even though the separations are followed by treatment of the metal residues with acids or with molten potassium bisulphate, again a sharp separation cannot be expected. In using such methods of separation, it often becomes necessary to combine the determinations of a number of separate fractions in evaluating the determination of a particular constituent.

The importance of hydrolytic reactions in analytical separations appears to have been given but little attention by chemists in the past. The reason for this may possibly be a lack of means for carefully controlling the pH of the solutions. It is evident that hydroxides of the platinum metals were known, but their significance in analysis does not seem to have been realized. The precipitation of hydrated tervalent rhodium oxide by alkalies and by alkali carbonates, for instance, was well known, but no use was made of the reaction in the analytical separation of rhodium. In the purification of platinum, Doebereiner [1] did propose a method by which the impurities were collectively precipitated by hydrolysis, using milk of lime. Claus,[2] however, pointed out that the elimination of impurities by this method was never complete. About 20 years ago, Mylius and Mazzucchelli [3] proposed a similar collective precipitation of impurities for use in the approximate analysis of platinum, except that an oxidizing reagent, sodium hypobromite, was added to a neutral or slightly alkaline solution to produce hydrated oxides of higher valence. Precipitation by hydrolysis was later studied by Wichers [4] in the development of an analytical method for the separation of rhodium from platinum and in the refining of platinum.[5] In the analytical separation, a definite alkalinity was established by the addition of an excess of freshly prepared barium carbonate. In the refining operation, precipitation was made in a solution slightly alkaline with sodium bicarbonate to which sodium bromate was added. These researches of Wichers

[1] Franz Doebereiner, Ann., vol. 14, pp. 17, 251, 1835.
[2] C. Claus, Bull. acad. sci., St. Petersburg, vol. 3, p. 38, 1845.
[3] F. Mylius and A. Mazzucchelli, Z. anorg. Chem., vol. 89, p. 1, 1914.
[4] E. Wichers, Jour. Am. Chem. Soc., vol. 46, p. 1818, 1924.
[5] E. Wichers, R. Gilchrist, and W. H. Swanger, Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

clearly demonstrated the value of hydrolytic reactions in the chemistry of the platinum metals.

The use of hydrolytic precipitation was further extended by Gilchrist in studies on the analytical separation and determination of ruthenium,[6 7] osmium,[8] and iridium.[9] In these studies, it was found that ruthenium is completely precipitated from a boiling solution having an acidity of pH 6;[10] that osmium is quantitatively precipitated between pH 1.5 and 6; and that iridium is entirely precipitated between pH 4 and 6.

Quite recently, Moser and Hackhofer[11] have reported on the separation of iridium from platinum, and Moser and Graber[12] on the separation of rhodium from platinum, by a hydrolytic procedure in which the alkalinity is fixed by the reaction between bromate and bromide ions. This reaction, however, appears to come to equilibrium so slowly that prolonged boiling and digestion is required to complete the precipitation.

The purpose of this paper is to present the results of the application of hydrolytic precipitation to the separation of rhodium from platinum, of iridium from platinum, of palladium from platinum, and of the collective separation of rhodium, iridium, and palladium from platinum. In addition, the paper contains the results of experiments on the determination of palladium, as well as its separation from rhodium and iridium, by means of dimethylglyoxime.

II. MATERIALS USED IN THE EXPERIMENTS

The platinum metals which were used throughout the investigation were purified by methods previously described[13] and were found to be free from impurities by spectrochemical analysis. In order to avoid errors incident to volumetric measurements, weighed portions of the ammonium salts of the chloro-acids of rhodium and of iridium were used. The compounds were carefully mixed by grinding in an agate mortar and their metallic contents determined by direct ignition of portions of the salts in hydrogen, whenever a series of samples was weighed. The metallic contents were never calculated from the theoretical compositions of the salts. With platinum and palladium, weighed portions of the pure metals in the form of foil were taken.

III. SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM

The simplest and most direct way to separate platinum from palladium, rhodium, and iridium is to precipitate collectively by hydrolysis the hydrated oxides of palladium, rhodium, and iridium. The method recommended for this separation is given below and is equally suitable for the separation of platinum from each of the other three metals when present singly with platinum.

[6] Gilchrist, B.S. Jour. Research, vol. 3, p. 993, 1929.
[7] Gilchrist, B.S. Jour. Research, vol. 12, p. 283, 1934.
[8] Gilchrist, B.S. Jour. Research, vol. 6, p. 421, 1931.
[9] Gilchrist, B.S. Jour. Research, vol. 9, p. 547, 1932.
[10] It is to be noted that the values of pH mentioned in this paper were determined by means of indicator solutions and were not corrected to correspond to readings of the hydrogen electrode.
[11] L. Moser and H. Hackhofer, Monatsh., vol. 59, p. 44, 1932.
[12] L. Moser and H. Graber, Monatsh., vol. 59, p. 61, 1932.
[13] See footnote 5, p. 292.

1. METHOD RECOMMENDED FOR THE SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM, EITHER COLLECTIVELY OR SINGLY

(a) PREPARATION OF THE SOLUTION

Evaporate the solution, containing platinum, palladium, rhodium, and iridium, to a moist residue on the steam bath in a 600-ml beaker. Add 5 ml of hydrochloric acid [14] and again evaporate, repeating this operation until nitroso-compounds are decomposed. Add 2 g of sodium chloride and 5 ml of hydrochloric acid and evaporate this time to dryness. Add 2 ml of hydrochloric acid and dilute the solution to 300 ml with water.

(b) HYDROLYTIC PRECIPITATION OF PALLADIUM, RHODIUM, AND IRIDIUM

Heat the resulting solution to boiling and add to it 20 ml of a filtered 10 percent solution of sodium bromate. Carefully add a filtered 10 percent solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the solution by allowing a drop of brom cresol purple indicator solution (0.04 percent) to run down the stirring rod into the drop which clings to it as it is lifted from the hot solution. Sufficient bicarbonate has been added when the color of the indicator changes from yellow to blue. At this stage, add 10 ml more of the bromate reagent and boil the solution gently for 5 minutes. Test the acidity of the solution again and adjust it to that specified above, if necessary. The tendency is for the pH of the solution to shift to the acid side of the indicator as hydrolysis of the platinum metal compounds progresses. Again add 10 ml of the bromate solution and boil gently for 15 minutes. During this treatment, the acidity of the hot solution should stay constant.

As a precautionary measure, it is well to test the acidity again at the end of the second boiling period. On removing the beaker from the source of heat, the precipitate which has been formed will settle quickly, leaving a yellow mother liquor containing the platinum. Filter [15] the solution. Pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker, without attempting to remove material which clings to the walls, and wash the precipitate with a hot 1 percent solution of sodium chloride. It is important that the acidity of the wash solution be tested before it is used because hydrated palladium dioxide is attacked somewhat by hot slightly acid solutions. A solution of sodium chloride whose acidity does not exceed that at which brom cresol purple indicator contained in it changes color can be safely used. If the precipitate is caught on filter paper, return the filter to the beaker and dissolve the hydrated dioxides in

[14] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; and sulphuric acid, the concentrated acid of specific gravity 1.84. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean one volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

[15] The solution may be filtered through paper. It is highly desirable, however, to avoid paper if the palladium, rhodium, or iridium is to be reprecipitated. Iridium dioxide, which dissolves much less readily than either palladium or rhodium dioxide, tends to stain the paper pulp and cannot always be removed by washing. The material of which the paper is composed undoubtedly reacts with acids to some extent and, as a consequence, small quantities of organic compounds of the platinum metals appear to be formed which are not easily hydrolyzed. The difficulties encountered with filter paper are avoided by using a porcelain filtering crucible, having glazed walls and a porous base. Such crucibles are made by the State Porcelain Works, Berlin, Germany. The ones used in this work were 45 mm in height, 40 mm in diameter at the top and had a capacity of 30 ml. While no information could be obtained regarding their degree of porosity, they bore the mark "A1" and were very satisfactory. No trace of the precipitates was ever detected to have escaped these filters. No doubt, glass crucibles of suitable porosity could also be used.

diluted hydrochloric acid (1 + 1). If the filtering crucible is used, place it with the stirring rod in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker. This may be done with a very small piece of filter paper and added to the beaker. Replace the watch glass and add from 10 to 20 ml of hydrochloric acid, pouring a portion of it into the crucible and the remainder into the beaker. Place the covered beaker on the steam bath. The rhodium and palladium compounds will dissolve quickly. The iridium compound will dissolve more slowly and may even require a drop of nitric acid to be added to the solution. Carefully lift the crucible with the stirring rod, wash it with water and place in in a 250-ml beaker. The porous bottom will be stained somewhat. Add about 5 ml of hydrochloric acid, again pouring a portion of the acid into the crucible. Cover the beaker with a watch glass and set it on the steam bath. This treatment will usually leach out the small quantity of metal chloride present in the porous bottom. This operation should be repeated once more with fresh acid, however, to insure complete removal of metal chloride.

Combine the leachings with the main portion of the solution, add 2 g of sodium chloride, and evaporate to dryness on the steam bath. Add 2 ml of hydrochloric acid, dilute the solution to 300 ml with water, and repeat the precipitation of the hydrated dioxides as directed above. Two such precipitations have been found sufficient to separate platinum from rhodium, palladium, and iridium.[16]

IV. DISCUSSION OF THE HYDROLYTIC PROCEDURE

The normal valence of rhodium in chloride solution is three; that of iridium, three or four; that of palladium, two; and that of platinum, owing to the conditions necessary to dissolve it, four.

When a solution of tervalent rhodium as halide or sulphate is neutralized, the rhodium precipitates as a yellow hydrated tervalent oxide. This compound does not settle well and has a tendency to become colloidal when washed. For these reasons, the quantitative handling of it is somewhat difficult. If, on the other hand, the rhodium is oxidized to the quadrivalent state, it can be precipitated as an olive-green hydrated dioxide which does settle rapidly and which displays no tendency to become colloidal. It was found that complete precipitation of the olive-green compound occurred at pH 6 in a boiling solution.

The precipitate of hydrated tervalent iridium oxide is somewhat flocculent and gelatinous, whereas the deep green hydrated dioxide is more granular and settles quickly from solution. It was found that the dioxide is completely precipitated from a boiling solution over a range of acidity, pH 4 to 6.

[16] In the experiments reported in section VIII of this paper, the ratio of platinum to rhodium was approximately 5 to 1, that of platinum to palladium 2.5 to 1, and that of platinum to iridium 1 to 1. The quantity of platinum present was usually about 250 milligrams. In the Pt–Rh separation, no platinum was found in the rhodium solutions after the second hydrolytic precipitation, and in only one of the five experiments was any rhodium detected in the platinum fractions. The quantity detected in this instance was less than 0.1 mg. In the Pt–Pd separation, no palladium was detected in the recovered platinum nor was any platinum found in the filtrates from the precipitation of the palladium with dimethylglyoxime. In the Pt–Ir separation, only one of the three platinum fractions appeared to contain any iridium. The amount of iridium, however, was much less than 0.1 mg. For certain work in which a high degree of accuracy in the platinum determination is not essential, a single hydrolytic precipitation may be sufficient. It must be borne in mind, however, that a small amount of platinum will contaminate the hydrolytic precipitate. When careful work is being done, it may be necessary to make a third hydrolytic precipitation, but only in unusual cases.

Hydrated palladium dioxide, obtained in the presence of bromate, is brown in color, is completely precipitated at pH 6, and likewise settles well from solution.

Owing to the possible interference of nitroso compounds, it is recommended that the solution first be evaporated several times with hydrochloric acid. On a number of occasions when solutions containing rhodium had not been so treated, a small amount of rhodium failed to precipitate on hydrolysis. When the solutions were evaporated with hydrochloric acid, complete precipitation was always obtained. Unless the solution contains a sufficient amount of sodium chloride, it should not be evaporated to dryness. A solution containing only rhodium chloride, for instance, when evaporated to dryness on the steam bath, forms brown scales which do not redissolve readily in water. If sodium chloride is present, a double salt is formed which is easily soluble.

In the precipitation of rhodium and of palladium, sodium bromate is added to the slightly acidified solution. This is done to prevent the precipitation of tervalent rhodium and bivalent palladium oxides when the bicarbonate is added. Some of the bromate is decomposed by the acid solution so that it is advisable to add this reagent at intervals. A hot solution of tervalent iridium can be neutralized to pH 6 without the formation of a precipitate. In the recovery of iridium from a pure solution, it is often convenient to neutralize to pH 6 before adding the bromate. As the bicarbonate solution is added to the acidified bromate solution, an olive-green precipitate appears with rhodium, a dark green one with iridium, and a brown one with palladium. These precipitates immediately redissolve, particularly those of rhodium and palladium, but, as the acidity is reduced, permanent precipitates form. The appearance of a coagulated precipitate is a convenient indication that the acidity of the solution is approaching the desired value, namely, pH 6. Owing to the deep color of the solution, the endpoint cannot be determined in the usual manner. A convenient method, however, consists in testing a drop of the hot solution, clinging to the stirring rod, with a drop of brom cresol purple indicator solution. The actual acidity of the solution will be slightly greater than that indicated by the drop. Experiments have repeatedly shown, however, that precipitation is quantitative at the acidity determined in this manner.

It sometimes happens that the salt used in preparing the wash solution contains a small amount of acid. Hydrated iridium dioxide can be safely washed with solutions as acid as pH 4. Hydrated rhodium dioxide, and more particularly the palladium compound, are attacked by slightly acid solutions and should be washed only with solutions which are practically neutral. It is well, therefore, to test the acidity of the wash solution before using it. A solution more acid than that which causes a change in color of brom cresol purple indicator contained in it should not be used.

V. DETERMINATION OF PLATINUM

The following procedure is recommended for the recovery and determination of platinum, after its separation from palladium, rhodium, and iridium.

Add 20 ml of hydrochloric acid to each of the cooled filtrates from the hydrolytic precipitation. Warm the solutions carefully until

they become quiescent. Combine the partially concentrated filtrates and then evaporate to dryness. To make certain that all of the bromate is decomposed, add 5 ml of hydrochloric acid and again evaporate. Dissolve the residue in 100 ml of water and filter the resulting solution. Wash the filter with diluted hydrochloric acid (1+99). Add 20 ml of hydrochloric acid and dilute the solution to 400 ml.

Precipitate the platinum as sulphide from a gently boiling solution by passing a rapid stream of hydrogen sulphide through it. Allow the solution to cool somewhat with the hydrogen sulphide still passing through it.

Filter the solution and wash the sulphide precipitate with diluted hydrochloric acid (1+99). Ignite the dried filter and precipitate in a porcelain crucible. Leach the metal residue with diluted hydrochloric acid, transfer it to a filter, and wash it thoroughly with hot water. Ignite the filter and metal again strongly in the air. It is usually customary to weigh the metal so obtained. A slight error will result, however, because sulphur cannot be entirely eliminated by ignition either in air or in hydrogen. The amount of sulphur retained by 0.25–g portions of platinum is usually less than 1 milligram.

In work of the highest accuracy, dissolve the metallic platinum obtained by ignition of the sulphide in aqua regia. Decompose nitroso compounds by adding hydrochloric acid and evaporating to a moist residue. Filter the solution into a clean, unetched beaker. Wash the filter with diluted hydrochloric acid (1+99). Dilute the solution to 100 ml, heat it to boiling, and add to it a solution containing 3 g of sodium acetate and 1 ml of formic acid for each 0.25 g of platinum present. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1 percent solution of ammonium chloride. Place the filter and the spongy metal in a porcelain crucible and ignite them strongly in the air. Leach and wash the ignited metal as previously directed. This precaution is taken to remove traces of soluble salts. Finally ignite the platinum again in air. It will now be free from sulphur. Weigh as metallic platinum.

In the determination of the platinum metals, by ignition of sulphide precipitates, a significant error may be caused by the retention of sulphur. It is well known that when palladium sulphide is ignited elimination of sulphur is very difficult to attain. In fact, if the sulphide is ignited rapidly enough, it will often fuse into a silvery globule. While the retention of sulphur by platinum is not nearly so marked as it is by palladium, a small but significant amount does remain when the sulphide is ignited in air. In 17 experiments, the weights of platinum recovered by ignition of the sulphide in air exceeded those taken by amounts which ranged from 0.0 to 1.1 mg and averaged 0.5 mg. In 14 of the 17 experiments, the platinum residues were recovered after separation from palladium, rhodium, and iridium. In the other three, pure platinum was dissolved in aqua regia and simply precipitated by hydrogen sulphide. These three residues were alternately ignited in air and in hydrogen. The excesses in weight dropped from 1.1 mg, 0.5 mg, and 0.7 mg to 0.6 mg, 0.2 mg, and 0.4 mg, respectively, by this treatment. These 3 residues and 4 others were then dissolved in aqua regia and the resulting solutions evaporated several times with hydrochloric acid. The solutions were filtered and to each of them

was added 5 drops of a filtered 10 percent solution of barium chloride. A precipitate of barium sulphate was obtained in each solution. No precipitate of barium sulphate was observed in blank solutions which contained the same quantities of nitric and hydrochloric acids.

Wichers,[17] a few years ago, found errors of the same magnitude, when similar quantities of platinum sulphide were ignited in air. When he charred and ignited the filters and precipitates extremely slowly, however, no significant errors were observed and the platinum residues were found to contain only a few hundredths of a milligram of sulphur. When he recovered the platinum with formic acid, the results were consistent with those reported in this paper. Wichers also extended his observations to the ignition of rhodium sulphide. He found no significant amount of sulphur in the resulting residues nor did he find that the manner of ignition, whether rapid or slow, affected the weight of the recovered metal. These conclusions were later confirmed by the writer.

VI. DETERMINATION OF PALLADIUM

Since the introduction of dimethylglyoxime as a precipitant for palladium by Wunder and Thüringer,[18] this organic compound has practically, if not entirely, displaced reagents formerly used, such as mercuric cyanide and potassium iodide. Wunder and Thüringer, according to their original articles, ignited the compound of palladium with dimethylglyoxime to metal for purposes of weighing. Soon, however, it became customary to weigh the dried compound as is done in the case of nickel.

The preparation of palladium in the metallic form suitable for weighing has always been attended by the difficulty which arises from the pronounced property of palladium to absorb hydrogen. When palladium is determined as metal, Swanger [19] recommended the decomposition of the dried glyoxime precipitate in a Rose crucible under hydrogen, followed by an ignition in air and another in hydrogen. In order to eliminate the absorbed hydrogen, he heated the crucible again in air for a moment, and finally reduced the slightly oxidized metal with formic acid on the hot plate. The treatment with formic acid often has to be repeated several times in order to produce a sponge which does not have a slight purplish color.

According to Wöhler,[20] palladium dioxide, PdO_2, cannot exist above 200 C, but decomposes into the monoxide, PdO, and oxygen. The monoxide, in turn, has a dissociation pressure of 760 mm at 877 C. Experiments showed that metallic palladium, silvery grey in color, can be obtained by simply igniting in carbon dioxide for 2 minutes the palladium which has been reduced in hydrogen. It was also found that the same result was obtained by igniting oxidized palladium in carbon dioxide. It was further found that simple strong ignition of oxidized palladium in the air formed the metal, which, however, took on a purplish color as it cooled to room temperature. The quantity of oxide thus formed was found to amount to only 0.1 mg with portions of palladium weighing 100 mg.

[17] Unpublished work by Edward Wichers.
[18] M. Wunder and V. Thüringer, Z. anal. Chem., vol. 52, pp. 101, 660, 740, 1913.
[19] W. H. Swanger, Analysis of Dental Gold Alloys, B.S. Scientific Papers No. 532, Aug. 11, 1926.
[20] L. Wöhler, Z. Elektrochem., vol. 11, p. 836, 1905.

Three experiments were made in which the glyoxime precipitate was caught on filter paper, washed with diluted hydrochloric acid (1 + 99), and finally with hot water. The filter containing the precipitate was wrapped in a second filter and charred carefully in the air. The residue was then ignited strongly in the air and the resulting oxidized palladium reduced in hydrogen. Finally, the metal was heated in carbon dioxide for 2 minutes and allowed to cool in an atmosphere of this gas. The quantities of palladium taken, in the form of foil, were 0.0994 g, 0.0992 g, and 0.1009 g. The metal residues weighed 0.0995 g, 0.0993 g, and 0.1010, respectively, no correction being made for the filter paper ash.

Experiments were also made in which the glyoxime compound itself was weighed. One of the precipitates was caught on an asbestos pad in a Gooch crucible and the other two in porcelain filtering crucibles. The precipitates were washed thoroughly with hot water and dried for 1 hour at 110 C. The quantities of palladium taken, in the form of foil, were 0.1061 g, 0.0954 g, and 0.0973 g. The glyoxime precipitates weighed 0.3348 g, 0.3014 g, and 0.3072 g. Using the theoretical factor for the percentage of palladium in the compound, namely, 0.3167, the calculated quantities of palladium recovered were 0.1060 g, 0.0954 g, and 0.0973 g, respectively.

In the preceding experiments, the palladium was precipitated from solutions of its chloride in diluted hydrochloric acid. Each solution had a volume of 350 ml and contained 10 ml of hydrochloric acid. No palladium was detected in the filtrates nor in the wash waters. In another experiment, the glyoxime precipitate was washed with 200 ml of hot water in order to determine whether it was appreciably soluble. No palladium was detected in the evaporated washings.

Other experiments showed that palladium was quantitatively precipitated by dimethylglyoxime not only from solutions of its chloride in diluted hydrochloric acid but also from solutions of its sulphate in diluted sulphuric acid. When the yellow precipitate was decomposed by nitric acid or by aqua regia, as is often done when palladium is to be reprecipitated, it was found that the metal was not always completely recovered. A small but significant amount of it remained in solution, which could be precipitated only after the filtrate had been heated until vapors of sulphuric acid were evolved.

VII. DETERMINATION OF RHODIUM AND OF IRIDIUM

Rhodium may be conveniently determined by igniting the hydrated dioxide to an anhydrous oxide in air and reducing the latter compound to metal in hydrogen. In order to prevent deflagration, the filter and precipitate are impregnated with ammonium chloride and carefully charred before they are strongly ignited in the air.

Rhodium may also be conveniently determined by igniting the sulphide to an anhydrous oxide and reducing the resulting oxide to metal in hydrogen. This method is recommended for the recovery and determination of rhodium after its separation from iridium by titanous chloride.[21] Rhodium is quantitatively precipitated by hydrogen sulphide from a gently boiling solution of its chloride in diluted hydrochloric acid, but it is only partially precipitated from a

[21] See footnote 9, p. 293.

solution of its sulphate in diluted sulphuric acid. A solution of the rhodium can be prepared, however, by adding diluted hydrochloric acid (1+2), equal to three times the volume of the concentrated sulphuric-acid solution, and boiling it. The yellow color of the sulphate solution then changes to rose-red, no doubt indicating a conversion of the sulphate to the chloride. No difficulty attends the precipitation of rhodium from the solution so treated.

Iridium is best determined by igniting its hydrated dioxide to an anhydrous oxide and then reducing the oxide in hydrogen. The same precaution must be used to prevent deflagration as was described for rhodium. Unfortunately, the precipitation of iridium from acid solutions by hydrogen sulphide is often incomplete and as yet the conditions suitable for quantitative precipitation have not been established.

VIII. EXPERIMENTAL RESULTS ON THE SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM

The method which is outlined in section III was used to effect the separation of platinum from palladium; the separation of platinum from rhodium; the separation of platinum from iridium; and the separation of platinum from these three metals when present together.

Owing to the difficulty encountered in the direct precipitation of the platinum from the hydrolytic filtrates by formic acid, the platinum was first precipitated by hydrogen sulphide. The ignited sulphide was redissolved and the platinum then precipitated by formic acid in a solution buffered with sodium acetate, as described in section V.

1. SEPARATION OF PLATINUM FROM PALLADIUM

The results of the determination of platinum and of palladium, starting with solutions containing both metals, are given in table 1. The hydrated dioxide of palladium from the second hydrolytic precipitation was redissolved in hydrochloric acid. The glyoxime precipitate was ignited in air, then in hydrogen, and finally in carbon dioxide. The palladium was determined as metal. No palladium was detected with dimethylglyoxime in the dissolved platinum residues nor was any platinum found, by means of ammonium chloride, in the filtrates from the precipitation of the palladium with dimethylglyoxime.

TABLE 1.—*Results of the analysis of solutions containing platinum and palladium*

Analysis no.	Platinum taken	Platinum recovered	Error	Palladium taken	Palladium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*
25–701	0.2848	0.2849	+0.0001	0.1044	0.1043	−0.0001
26–702	.2793	.2794	+.0001	.1243	.1243	.0000

If palladium alone is to be separated from platinum, a single hydrolytic precipitation, followed by a single precipitation with dimethylglyoxime, is undoubtedly sufficient to effect complete

separation. Complete separation of the two metals can also be accomplished, no doubt, by a double precipitation with dimethylglyoxime alone, provided that certain precautions are observed. Wunder and Thüringer,[22] operating in a hot solution, encountered difficulty in separating palladium from platinum with dimethylglyoxime, but Davis [23] later showed that if palladium is precipitated in a cold solution two precipitations as the glyoxime compound remove the platinum. Swanger [24] subsequently followed the procedure of Davis with excellent results. It should be borne in mind, however, that, if the palladium is reprecipitated from a solution of the first precipitate in nitric acid or in aqua regia, a small amount of palladium may remain in solution.

2. SEPARATION OF PLATINUM FROM RHODIUM

The results of the determination of platinum and of rhodium, starting with solutions containing both metals, are given in table 2. The rhodium was recovered by precipitation with hydrogen sulphide and determined as metal.

TABLE 2.—*Results of the analysis of solutions containing platinum and rhodium*

Analysis no.	Platinum taken	Platinum recovered	Error	$(NH_4)_3RhCl_6$ taken	Rhodium present [1]	Rhodium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*	*g*
9-646	0.2450	[2] 0.2454	+0.0004	0.1537	0.0469	0.0468	−0.0001
10-647	.2350	[2] .2350	.0000	.1682	.0513	.0512	−.0001
18-652	.2469	.2469	.0000	.0953	.0291	.0291	.0000
19-653	.2479	.2479	.0000	.0800	.0244	.0243	−.0001
20-654	.2617	.2618	+.0001	.0968	.0295	.0296	+.0001

[1] Calculated on the basis of an experimentally determined rhodium content of 30.50 percent.
[2] Pt determined by ignition of sulphide.

NOTE.—In analyses nos. 9-646 and 10-647, filter paper was used to catch the hydrated dioxide. In the other 3 experiments, the porcelain filtering crucible was used. In none of the 5 rhodium solutions, previous to the recovery of rhodium, was any platinum detected. The test for platinum was made as follows: The second hydrolytic precipitate of rhodium dioxide was dissolved in hydrochloric acid and the resulting solution evaporated to a moist residue on the steam bath. 5 ml of hydrochloric acid was added and the solution diluted somewhat and filtered. The filter was washed with diluted hydrochloric acid (1+99). The rhodium solution was then evaporated to a small volume and to it was added 10 drops of a saturated solution of ammonium chloride and 2 or 3 drops of nitric acid. The solution was next carefully evaporated to dryness on the steam bath. The dry salt mixture was dissolved in the smallest quantity of water possible and allowed to stand for one half hour. In the solutions tested, no precipitate of ammonium chloroplatinate appeared, whereas, in solutions of known platinum content 0.1 mg of platinum was readily detected and a precipitate was formed with 0.05 mg of platinum. A very faint trace of rhodium was detected in the final platinum residue of analysis no. 10-647. No rhodium was detected in the other 4 platinum residues. The test for rhodium was made as follows: The platinum residues were dissolved in aqua regia, the solutions were evaporated to a sirup with hydrochloric acid, and the bulk of the platinum was precipitated with ammonium chloride. The mother liquors and the wash waters containing ammonium chloride were evaporated to dryness. An extremely small amount of rhodium, if present, produces under these conditions a greenish discoloration of the small amount of ammonium chloroplatinate which has been carried along with the wash waters.

In determining rhodium, when it alone has been separated from platinum, it may be more convenient to catch the precipitate from the second hydrolysis on filter paper. The hydrated dioxide of rhodium can be ignited to metal in the same manner as iridium dioxide. If palladium or iridium is present with the rhodium, it is recommended that the rhodium be recovered, after its separation from these metals, by precipitation with hydrogen sulphide.

[22] See footnote 18, p. 298.
[23] C. W. Davis, Separation of Palladium from Platinum by Means of Dimethylglyoxime, Bur. Mines Reports of Investigations, serial no. 2351, May 1922.
[24] See footnote 19, p. 298.

3. SEPARATION OF PLATINUM FROM IRIDIUM

The results of the determination of platinum and of iridium, starting with solutions containing both metals, are given in table 3. The iridium was recovered by hydrolytic precipitation and determined as metal.

TABLE 3.—*Results of the analysis of solutions containing platinum and iridium*

Analysis no.	Platinum taken	Platinum recovered	Error	$(NH_4)_2IrCl_6$ taken	Iridium present [1]	Iridium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*	*g*
21–611	0.2359	0.2358	−0.0001	0.4500	0.1944	0.1945	+0.0001
22–612	.2692	.2694	+.0002	.4721	.2039	.2040	+.0001
23–613	.2501	.2501	.0000	.5684	.2455	.2456	+.0001

[1] Calculated on the basis of an experimentally determined iridium content of 43.20 percent.

NOTE.—The filtrates from the precipitation of platinum by hydrogen sulphide and by formic acid were heated until vapors of sulphuric acid were evolved and tested for iridium by adding nitric acid. In this test, with quantities of iridium less than 0.1 mg, the color developed is green, with larger amounts it is blue. Owing to the incomplete precipitation of iridium by hydrogen sulphide and by formic acid, iridium, if present with the platinum, will appear in the filtrates from these precipitations, at least partially. The filtrates from analysis no. 21–611 showed the presence of a quantity of iridium much less than 0.1 mg. No iridium was detected in the filtrates from the other 2 experiments.

4. SEPARATION OF PLATINUM FROM THE THREE METALS, PALLADIUM, RHODIUM, AND IRIDIUM

Critical experiments were made in which palladium, rhodium, and iridium were simultaneously precipitated as hydrated dioxides in the presence of platinum. The resulting platinum filtrates were carefully examined for palladium, rhodium, and iridium and the absence of these metals was established. The third hydrolytic filtrate gave no evidence of the presence of platinum, when treated with ammonium chloride.

That no platinum contaminated the second hydrolytic precipitate of the mixed dioxides of rhodium and iridium was shown by the following experiment: From a solution containing 0.2642 g of platinum, 0.1385 g of iridium, and 0.0465 g of rhodium, 0.0464 g of rhodium was recovered after its separation from iridium by treatment with titanous chloride, as described in a previous publication.[25] The ash of the paper used to filter the solution of rhodium sulphate, produced by dissolving the metallic rhodium from the second precipitation with titanous chloride, was found to contain no platinum. If platinum had contaminated the hydrolytic precipitate, it would have appeared, at least in part, at this point in the analysis.

IX. SEPARATION OF PALLADIUM FROM RHODIUM AND IRIDIUM

In one of their papers Wunder and Thüringer [26] reported on the separation of palladium from rhodium and from iridium, by means of dimethylglyoxime.

Preliminary experiments in this laboratory showed that palladium, when precipitated by dimethylglyoxime from a solution of the mixed precipitate of hydrated dioxides in diluted hydrochloric acid, was not contaminated by either rhodium or iridium. Apparently, a single precipitation of the glyoxime compound sufficed to effect a clean

[25] See footnote 9, p. 293.
[26] M. Wunder and V. Thüringer, Z. anal. Chem., vol. 52, p. 660, 1913.

separation. To confirm this observation, two solutions were prepared containing in the one, 0.2300 g of iridium, 0.0177 g of rhodium and 0.0342 g of palladium, and in the other, 0.2154 g of iridium, 0.0112 g of rhodium and 0.0333 g of palladium.

The palladium precipitates were caught on filter paper, washed with diluted hydrochloric acid (1 + 99), and finally with hot water. The filters and precipitates were placed in 500-ml erlenmeyer flasks and decomposed by treatment with 5 ml of sulphuric acid to which portions of nitric acid were added. After destruction of organic matter, the solutions were heated until heavy vapors of sulphuric acid were evolved. The solutions were then diluted somewhat and filtered. The filters were washed with diluted hydrochloric acid (1 + 99) and with water. The palladium compound was precipitated a second time from a volume of 350 ml and collected in porcelain filtering crucibles. It was thoroughly washed with hot water, dried at 110 C and weighed. The weights of the dried precipitates were 0.1080 g and 0.1051 g, respectively. The calculated quantities of palladium present, using the theoretical factor 0.3167, were 0.0342 g and 0.0333 g.

The filtrates from the second precipitation of the palladium were carefully examined for iridium, by heating them until vapors of sulphuric acid were evolved and adding nitric acid. No iridium was detected in them nor did any rhodium appear to be present, since the solutions remained colorless.

X. SEPARATION OF RHODIUM FROM IRIDIUM

The two metals of the platinum group which remain after the isolation of osmium, of ruthenium, of platinum, and of palladium are rhodium and iridium. These two metals can be separated from each other and determined by the procedure which is described in detail in a previous paper.[27]

Briefly, the method of separation consists in making two precipitations of the rhodium with titanous chloride from a hot solution of the metal sulphates in diluted sulphuric acid (5 + 95). The iridium is recovered from the resulting filtrates, after the removal of titanium with cupferron, by hydrolytic precipitation and determined as metal. The rhodium is recovered by precipitation with hydrogen sulphide, in a solution of the metal sulphate which has been boiled with hydrochloric acid, and is determined as metal.

The determination of rhodium and of iridium can be greatly simplified and the cupferron precipitations avoided if the solution can be divided conveniently into aliquot parts. Since the hydrated dioxides of rhodium and iridium are quantitatively precipitated under the same conditions, the two can be precipitated together and finally recovered as a metallic mixture. In addition, rhodium must be determined separately in a different portion of the solution.

In a forthcoming paper the various procedures of separation and determination which have been developed in this laboratory will be combined into a general scheme of analysis for the platinum group as a whole.

The writer wishes to express his appreciation to Edward Wichers for many helpful suggestions.

WASHINGTON, *December 14, 1933.*

[27] See footnote 9, p. 293.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP656

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AN EXAMINATION OF WATER FROM VARIOUS NATURAL SOURCES FOR VARIATIONS IN ISOTOPIC COMPOSITION

By Edward W. Washburn and Edgar R. Smith

ABSTRACT

The densities of samples of water from various natural sources have been measured in an effort to detect differences in isotopic composition. Small differences have been found in the following cases: After the removal of all non-aqueous constituents, the water of the ocean, of the Dead Sea, and of Great Salt Lake is denser than pure normal water by about 2, and the water of crystallization of native borax tetrahydrate, kernite ("rasorite"), by about 7 parts per million. The sap water from a young willow tree was heavier than normal water by 2.8 and the water produced by burning the dry wood was heavier by 5.4 parts per million.

A differential pycnometer method for measuring differences in density with a precision of 1 part in 1,000,000 is described.

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I. INTRODUCTION

Following the discovery that upon electrolysis of water the residue is enriched in the H^2 isotope of hydrogen,[1] it was found that the density, index of refraction, freezing point, boiling point, and vapor pressure of water thus changed in isotopic composition undergo corresponding changes [2 3] and furthermore, that fractional distillation [4 5] and adsorption [4] effect changes in the isotope ratio. It therefore appeared reasonable to expect that some isotopic fractionation of water may be taking place in nature during certain life processes, such as diffusion through animal membranes and transpiration through the leaves of plants, and may have occurred to a considerable extent

[1] E. W. Washburn and H. C. Urey, Proc. Nat. Acad. Sci., vol. 18, p. 496, 1932.
[2] E. W. Washburn, E. R. Smith, and M. Frandsen, Jour. Chem. Physics, vol. 1, p. 288, 1933.
[3] G. N. Lewis and R. T. Macdonald, Jour. Am. Chem. Soc., vol. 55, p. 3057, 1933.
[4] E. W. Washburn and E. R. Smith, Jour. Chem. Physics, vol. 1, p. 426, 1933.
[5] G. N. Lewis and R. E. Cornish, Jour. Am. Chem. Soc., vol. 55, p. 2616, 1933.

throughout past ages by such physical processes as the slow evaporation of inland seas. It also seemed possible that some fractionation of the hydrogen isotopes might have occurred during the formation of coal deposits and of petroleum.

The relative abundance of the H^2 isotope in hydrogen from a few natural sources, namely, water from the crater of Mount Kilauea, water from an obsidian, Devonian water, and helium-bearing natural gases, has been determined by spectroscopic comparison with ordinary laboratory distilled water without the detection of any differences.[6]

The density of water has been found to be quite sensitive to variations in isotopic composition [7] and in this work water from a variety of natural sources has been investigated for such variations by means of measurements of density.

II. A DIFFERENTIAL METHOD OF MEASURING DIFFERENCES IN DENSITY

The method used for determining small differences in density has been outlined briefly in a previous paper.[7] However, it is believed that the precision, simplicity of manipulation, and probable value of the method for other purposes [8] warrant a more complete description.

Two silica pycnometers very closely the same in size and weight, and of the shape shown in figure 1, are used. The capillary stem of each has a reference mark less than 0.01 cm in thickness, made with a diamond point, and the volume per unit length of the capillary is determined with an accuracy of 0.1 percent by calibration with mercury. The volume of each pycnometer up to the reference mark is determined with an accuracy of 0.1 percent by weighing empty, filling with distilled water to any suitable height in the capillary, as read with a cathetometer while the pycnometer is in a water thermostat, again weighing, and applying a correction for the volume of water in the capillary above the mark.

In making a measurement of the difference in density between a given sample and normal water, the first pycnometer is filled with normal water and the second with the sample, to any suitable heights in the capillaries. The filling is conveniently done with a fine silver capillary and the aid of a low vacuum line, as illustrated in figure 2. The pycnometers are then placed side by side, with their ground stoppers loosely in place, in a thermostat containing distilled water and having front and back of plate glass. After thermal equilibrium is attained, the height of the meniscus above the reference mark in each capillary is read with the cathetometer. The pycnometers are next taken out of the bath, wiped dry, placed on opposite pans of a balance with their stoppers tightened in place, and the difference in their weights is determined. After the weighing, they are emptied and refilled so that the first pycnometer now contains the sample water and the second contains normal water. Again they are placed in the thermostat in the same positions as before and the capillary heights recorded. They are again taken out, dried, placed on the

[6] C. A. Bradley and H. C. Urey, Phys. Rev., vol. 40, p. 889, 1932.
[7] E. W. Washburn, E. R. Smith, and M. Frandsen, B. S. Jour. Research, vol. 11, p. 453, 1933.
[8] For example, the measurement of partial molal volumes in dilute solutions.

same balance pans and the second difference in weight determined. The expression for the difference in density is obtained as follows:

Let P_1 = weight of pycnometer no. 1.
P_2 = weight of pycnometer no. 2.
V_1 = volume of pycnometer no. 1 to the reference mark.
V_2 = volume of pycnometer no. 2 to the reference mark.
D = density of sample investigated.
D_o = density of normal water.
$\Delta V_1'$, $\Delta V_1''$, $\Delta V_2'$, $\Delta V_2''$ = volume of water above the reference mark in the capillary of pycnometer no. 1 in the first and second fillings and pycnometer no. 2 in the first and second fillings, respectively.

m_1 = difference in masses after the first filling.
m_2 = difference in masses after the second filling.

FIGURE 1.—*Silica pycnometer.*

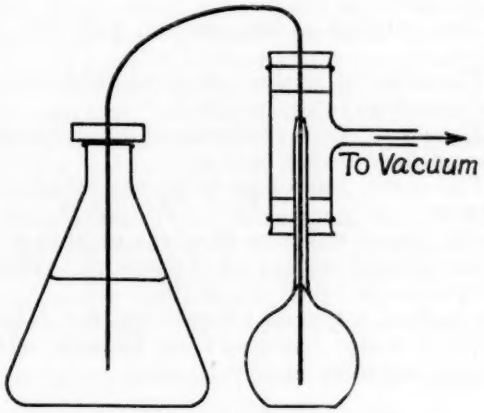

FIGURE 2.—*Device for filling pycnometer.*

If no. 1 is always placed on the right hand pan of the balance,

$$P_2 + V_2D + \Delta V_2'D = P_1 + V_1D_o + \Delta V_1'D_o + m_1 \quad (1)$$

$$P_2 + V_2D_o + \Delta V_2''D_o = P_1 + V_1D + \Delta V_1''D + m_2 \quad (2)$$

Subtracting equation (2) from equation (1) and rearranging gives

$$(V_1 + V_2)(D - D_o) = (m_1 - m_2) + (\Delta V_1'D_o - \Delta V_1''D) - (\Delta V_2'D - \Delta V_2''D_o)$$

Since this method is used only for the measurement of small differences in density, where $D - D_o < 0.001$, the equation can be written

$$D - D_o = \frac{(m_1 - m_2) + D_o[(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')]}{V_1 + V_2} \quad (3)$$

For most of the measurements made during this investigation a bulb volume of about 50 cm³ and a capillary diameter of about 0.1 cm were found suitable. For a precision in $D - D_o$ of one part in one million with pycnometers of this size, a convenient distribution of precision in the measurements is:

1. The temperature of the stirred water in the thermostat is held constant to within 0.01°, for with extreme fluctuations of the thermostat temperature less than 0.01°, the lag in the pycnometers is sufficient to maintain them constant to within 0.002°.
2. The capillary heights are read to 0.001 cm.
3. The weighings are made to 0.03 mg.

It is advantageous to adjust the capillary heights to make the correction $(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')$ small and thus avoid the necessity for a very precise calibration of the capillaries. It is to be noted that:

1. The dry weights of the pycnometers are not required.
2. The pycnometers are so closely alike that effects of varying humidity are balanced.
3. The temperature of the thermostat need not be accurately known but should be constant and uniform while the pycnometers are in the bath.
4. The effect of barometric and hydrostatic pressure on the capillary heights is balanced.
5. The (negligible) evaporation past the ground glass stoppers is balanced.
6. The silica bulbs show no measurable temperature hysteresis over the temperature range involved.
7. The small effect of dissolved air is balanced and it is not necessary to prepare air-free water.
8. The correction for air buoyancy affects only the difference of the differences, $(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')$, in the capillary volumes and with proper adjustment of the heights is negligible.
9. No unusual apparatus or particular skill is required for measurements precise to 1 part in 1 million.

The data of a typical experiment, the determination of $D - D_0$ for a sample of water prepared from Kernite, native borax tetrahydrate, are shown in tables 1 and 2.

TABLE 1.—*Cathetometer readings for the first filling*

No. 1 filled with normal water			No. 2 filled with the sample water		
Meniscus	Graduation mark	Capillary height	Meniscus	Graduation mark	Capillary height
75.651	70.866	4.785	75.774	70.658	5.116
75.656	70.869	4.787	75.777	70.658	5.119
75.650	70.867	4.783	75.773	70.657	5.116
75.654	70.868	4.786	75.773	70.657	5.116
Average		4.785 cm	Average		5.117 cm
Avg deviation		0.0013	Avg deviation		0.0013

TABLE 2.—*Cathetometer readings for the second filling*

No. 1 filled with the sample water			No. 2 filled with normal water		
Meniscus	Graduation mark	Capillary height	Meniscus	Graduation mark	Capillary height
75.439	70.864	4.575	75.249	70.653	4.596
75.438	70.865	4.573	75.248	70.656	4.592
75.440	70.864	4.576	75.249	70.653	4.596
75.438	70.864	4.574	75.249	70.654	4.595
Average		4.575 cm	Average		4.595 cm
Avg deviation		0.0010	Avg deviation		0.0013

The calculation of $D-D_o$ is made as follows:

Difference in weight after first filling, $m_1 = 3.79463$
Difference in weight after second filling, $m_2 = 3.79111$

$$m_1 - m_2 = 0.00352 \text{ g}$$
$$(\Delta V_1' - \Delta V_1'') = (4.785 - 4.575)0.00843 = 0.00177$$
$$(\Delta V_2' - \Delta V_2'') = (5.117 - 4.595)0.00861 = 0.00449$$
$$(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'') = -0.00272 \text{ cm}^3$$
$$-0.00272\, D_o = -0.00271 \text{ g}$$
$$D - D_o = (0.00352 - 0.00271)/112$$
$$= 0.000,0072 \text{ g/cm}^3, \text{ or } 7.2 \text{ ppm.}$$

III. THE SAMPLES OF WATER EXAMINED

The water obtained or prepared from each source, after appropriate preliminary treatment such as distillation for the removal of salts or refluxing with strong alkaline permanganate to destroy large amounts of organic matter, was purified by (1) distillation from alkaline permanganate, (2) distillation from dilute phosphoric acid, (3) simple distillation, rejecting first and last portions in each distillation. Laboratory distilled water, used as the normal water for comparison, was subjected to the same treatment. The source of this water was the Potomac river. Lamb and Lee,[9] who have made precise measurements of the density of normal water purified by methods similar to those used by us, found that the densities of different lots of such water differed by less than one part per million.

A description of the samples and the experimental results follow. Where it is stated that a sample was found to be of normal density, it is meant that the density is not different by more than one part in one million from that of normal water at 25 C.

1. Water prepared from cows' milk had the same density as normal water.

2. Water prepared from slaughter-house blood was found to be of normal density.

3. Thirty liters of laboratory distilled water were reduced to 225 ml by transpiration through growing plants (cowpeas and willows). After purification, this final residue had the density of normal water. In a second experiment involving practically the same volume change but at a greater transpiration rate, with the growth of willows, no difference was found.

4. A sample of brine from approximately the 60-foot level of Searles Lake was supplied by the American Potash & Chemical Corporation, Trona, Calif. Searles Lake is subject to spring and winter rains so that no large effect due to evaporation was expected. No density difference was found.

5. Dr. Bernard N. Moore supplied a sample of water from the Salton Sea, collected about 5 miles south of Travertine Point. This water was found to be of normal density.

6. The Intermountain Experiment Station of the Bureau of Mines, Salt Lake City, Utah, supplied a sample of water from Great Salt Lake collected at a point where it was not diluted by the immediate entry of fresh water. Two determinations with intermediate redistil-

[9] A. B. Lamb and R. E. Lee, Am. Chem. Soc., vol. 35, p. 1681, 1913.

lation gave values of $D-D_o$ equal to 2 and 3.4 parts per million, an average of 2.7 ± 0.7 ppm.

7. Surface water from the Dead Sea collected at a point 5 or 6 miles from the mouth of the River Jordan was obtained through the American Consular Service, Jerusalem, Palestine. The results of three measurements were 1.5, 2.2, and 2.7, with an average of 2.1 ± 0.5 ppm. for $D-D_o$. The water was redistilled between the second and third measurements.

8. Dr. Paul Bartsch supplied a sample of ocean water taken 3,000 meters below the surface, (lat. 19°13′ N., long. 65°16′ W.). It had a salinity of 34.88 parts per thousand, as determined by Dr. R. C. Wells. This water was found to be denser than normal water by 2 ppm.[10]

9. Two species of native borax crystals, kernite, the tetrahydrate ("rasorite"), and the decahydrate ("tincal") were obtained from the Pacific Coast Borax Co., Kramer Station, Hinkley, Calif. The results of two measurements, with intermediate distillation, on the water obtained from a single large crystal of kernite were 7.2 and 6.6 ppm heavier than normal water. To check this interesting discovery, water from a different lot of smaller broken crystals of kernite was measured and found to be 6.7 ppm heavier than normal. The average of the three determinations is 6.8 ± 0.2 ppm. The water from the "tincal" crystals however, exhibited no difference in density from normal water.

10. Water prepared by M. Frandsen of this laboratory by combustion of a sample of dry anthracite coal was found to be of normal density.

11. Water prepared by Frandsen by burning natural propane with commercial oxygen was also found to be of normal density.

12. Water prepared by M. Frandsen, from the sap content of branches and leaves of a young willow tree, was found to be 2.8 ppm heavier than normal water (two determinations with intermediate distillation, 2.8 and 2.8).

13. Water prepared by M. Frandsen, by combustion (in dry oxygen) of the dry wood and leaves from the above experiment, was found to be 5.4 ppm heavier than normal water (two determinations, 5.5 and 5.2).

14. The possibility of fractionation by a selective action of iron on dilute acid was tested by examining a sample of water prepared from pickling acid, furnished by John A. Roebling's Sons Co., Roebling, N.J. No effect was found.

15. Any process involving the electrolytic separation of hydrogen from an aqueous solution would be expected to increase the density of the residual water. Newell and Ficklen[11] have reported density increases of from 20 to 640 parts per million in samples of water from nine chromium plating baths. As a matter of interest, water from two chromium plating baths in use at the United States Bureau of Engraving and Printing was tested. One sample was found to be heavier than normal water by 2 and the other by 5 parts per million.

[10] The first determination on the ocean water indicated a density excess of not more than 1 ppm. Having learned that Gilfillan (Jour. Amer. Chem. Soc., March 1934) working at O C had found a density excess of 2 ppm for ocean water, we repeated our measurements and obtained results which confirmed his determination.

[11] I. L. Newell and J. B. Ficklen, Jour. Am. Chem. Soc., vol. 55, p. 2167, 1933.

IV. DISCUSSION

In this investigation the only natural sources of water found to have an isotopic composition differing appreciably from normal were (1) those which have been subjected to evaporation over many centuries, and (2) the sap water of a willow tree and the water obtained by burning the dry wood. The water of crystallization of native borax (kernite) probably represents almost the last portion of water left from the complete evaporation of an inland sea. The existence of a natural source of hydrogen having an isotopic ratio differing from normal by more than 0.0001 appears improbable.

V. SUMMARY

A search has been made for natural water having an isotopic composition differing from normal. Purified samples of water prepared from milk, blood, the residue from the transpiration and growth of plants, sap from a willow tree, brine from Searles Lake, the Salton Sea, Great Salt Lake, the Dead Sea, ocean water, water of crystallization of native borax, water from the combustion of anthracite coal, of willow wood, and of propane, have been tested by a differential density method, which is described. Water from the ocean, from Great Salt Lake, and from the Dead Sea is heavier than normal water by two parts per million. The water of crystallization of native borax tetrahydrate (kernite) is heavier by seven parts per million. The sap water from a young willow tree was heavier than normal water by 2.8 and the water produced by burning the dry wood was heavier by 5.4 parts per million. No differences were found for the other samples.

WASHINGTON, January 15, 1934.

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SOME EXPERIMENTS WITH PURE-METAL RESISTANCE STANDARDS

By James L. Thomas

ABSTRACT

National standardizing laboratories use wire-wound standards for maintaining the unit of electrical resistance. The material for these standards is usually manganin—an alloy of copper, nickel, and manganese. This alloy corrodes rather readily and in general its resistance does not remain as constant as is desired. It is believed that coils of pure metals, especially the noble metals, will be more stable in resistance and might be used to maintain the unit. Pure-metal standards have been constructed of copper, silver, tin, gold, and platinum wire, and measured at the ice point. The gold and platinum coils have been very stable in resistance. The construction, method of measurement, and results are given.

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I. INTRODUCTION

Until about the middle of the nineteenth century there was no widely accepted system of electrical units, and each experimenter used such units as were convenient for the work he was doing. As a result, the first standards of electrical resistance were copper or iron wires of stated dimensions. About 1860 Siemens [1] proposed as a unit the resistance at 0 C of a uniform column of mercury one meter

[1] Siemens, Phil. Mag., vol. 21, p. 25, 1861.

in length, having a cross section of one square millimeter. This "Siemens unit" had the advantage of being readily reproducible, and soon came into rather general use. In England, however, it was soon superseded by an "absolute unit" based upon measurements made in 1862 and 1863 under the direction of a committee of the British Association for the Advancement of Science.[2] This unit, known as the B.A. unit, was preserved by means of a group of coils constructed for the most part of precious-metal alloys.

Since about 1890 the place of precious-metal alloys has been taken largely by manganin, an alloy of copper, nickel, and manganese. It would seem, a priori, that the change in materials for the construction of resistance standards has proceeded in the wrong direction. The most important consideration in the choice of a material for primary standards is undoubtedly that of stability. It is to be expected that alloys will be less stable in composition, and hence in resistance, than pure metals, as they are more liable to changes in structure than are pure metals. Also, the base metals are more subject to surface action than the noble metals. There is, moreover, a little direct experimental evidence in favor of the use of pure metals.

Between 1862 and 1864 Matthiessen [3] investigated the stability of the resistance of a number of pure metals and alloys. From this investigation he concluded that, in addition to certain alloys, both gold and platinum would be satisfactory for use in the construction of resistance standards, and that silver and copper would not remain constant. On the basis of these results there were included two coils of platinum when in 1865 he constructed the standards for the preservation of the B.A. unit. These coils have remained in the possession of the British Association for the Advancement of Science and have been compared with one another and with the other B.A. coils by a number of observers. Nearly 70 years after their construction, Glazebrook and Hartshorn [4] concluded that probably there had been no change in the resistance of the platinum coils, and they used the platinum coils as a basis for discussing the stability of the remaining B.A. coils, made of alloys.

While the accuracy with which the platinum coils have been measured has been limited to a certain extent by their large temperature coefficients and method of mounting, their performance seemed to justify additional experiments with pure-metal resistance standards.

To obtain reasonably definite information concerning the stability of pure-metal standards, the resistance measurements should, if possible, be made with a precision of 1 part in 1,000,000. This requires that the temperature at which the measurements are made be reproducible to within 0.0002° C. This paper discusses the various problems involved in the design, construction, and measurement of pure-metal resistance standards. Data extending over a period of nearly 2 years are given for standards constructed of copper, silver, tin, gold, and platinum wire.

[2] Report of the Committee on Standards of Electrical Resistance; British Association Report, p. 345, 1864.
[3] A. Matthiesen, British Association Report, p. 351, 1864.
[4] Glazebrook and Hartshorn, British Association Report, p. 417, 1932.

II. SUITABLE TEMPERATURE FOR MEASUREMENT OF PURE-METAL STANDARDS

As stated above, in order to measure their resistance to 1 part in 1,000,000, the temperature at which the pure-metal standards are measured should be reproducible to within 0.0002° C, although the actual temperature need not be known. It is undoubtedly out of the question to immerse the standards in an oil bath and control and measure the temperature to anywhere near this accuracy.

In selecting a reproducible temperature for this purpose, one would probably consider first the ice point. This temperature, however, is a function of the conditions under which the ice is melted. There is a small change in the ice point with pressure, amounting to about 0.0001° C for a change in pressure of 1 centimeter of mercury. The ice point also depends upon the kinds and amounts of dissolved gases, the difference in the ice point for saturated and air-free ice being about 0.002° C.[5] However, it would be expected that a temperature variation of much less than 0.002° C would result from variations in the amount of dissolved air, as saturation probably takes place very rapidly and a reproducible condition is probably soon reached.

In 1927, Michels and Coeterier [6] investigated the triple point of water and suggested its use as a fixed point on the temperature scale instead of the usual ice point. Their investigation was conducted by means of a resistance thermometer and the triple point was found to be reproducible to better than 0.001° C. A more careful investigation was made by Moser [7] in 1929 at the Physikalisch-Technische Reichsanstalt, also using a resistance-thermometer method, and he reported the temperature to be reproducible to about 0.00005° C. This was probably the limit of accuracy of his determinations.

Moser's work showed that the triple point of water was suitable as a temperature at which to measure pure-metal resistance standards within 1 part in 1,000,000. However, for the present work, it was decided first to investigate the stability of pure-metal resistance standards when measured at the ice point. If they showed sufficient promise, arrangements would be made to compare the temperature of the different ice baths with that of the triple point.

III. CONTAINER FOR PURE-METAL COILS

Since the containers for the pure-metal coils were to be immersed in an ice bath, provision had to be made to prevent the bath from electrically short-circuiting the leads connecting to the ends of the resistance coils. Also it was necessary to select containers through which the heat developed by the test current would be very readily conducted to the ice bath. For the latter reason it did not seem possible to seal the coils in glass containers.

It was decided to make the containers of two thin coaxial brass tubes, practically the same as those described in Bureau of Standards Journal of Research, volume 5, page 295, 1930. The only essential change was to braze small conduits to the inner walls of the container,

[5] Foote and Leopold, Amer. Jour. Sci., vol. 11, p. 42, 1926.
[6] Michels and Coeterier, Proc. K. Ak. v. Wetensch. Amsterdam, vol. 30, p. 1017, 1927.
[7] Moser, Annalen der Physik, vol. 393, p. 341, 1929.

round the holes through which are brought the current and potential leads. These conduits extend several inches out of the double-walled container, and the hard-rubber terminal blocks are mounted on the end of these tubes instead of being attached to the double-walled containers. The leads are insulated from each other and from the surrounding brass conduits through which they pass up to binding posts on the terminal block. A cross section of the container is shown in figure 1.

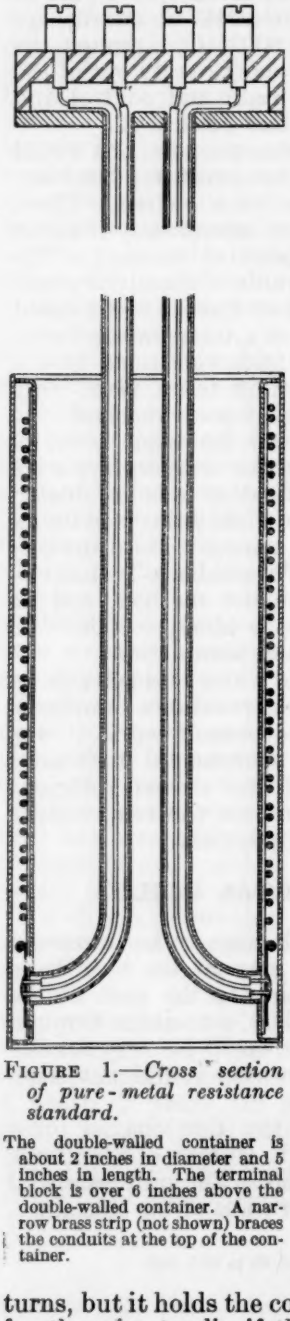

FIGURE 1.—*Cross section of pure-metal resistance standard.*

The double-walled container is about 2 inches in diameter and 5 inches in length. The terminal block is over 6 inches above the double-walled container. A narrow brass strip (not shown) braces the conduits at the top of the container.

The double-walled part is slightly over 2 inches (5 cm) in diameter and about 5 inches (13 cm) long. The over-all length of the standards is about 12 inches (30 cm). This allows the standards to be inserted in the ice bath contained in a wide-mouth thermos bottle, with the terminal block remaining above the thermos bottle. The conduits are in contact with the ice for a considerable length, so it is not probable that a sufficient amount of heat is conducted down along them, or through the leads, to appreciably affect the resistance.

As the pure-metal coils are very soft after annealing, it is almost impossible to anneal them on a mandrel and transfer them to the containers, as was done in the case of manganin coils. For this reason the inner tubes are insulated with a layer of mica about 0.001 inch (0.025 mm) thick, upon which the wires are wound, using a lathe to space them properly. Since the mica is not damaged by being heated to 600 C, the inner tube with the coil and insulation may be inserted in a furnace and annealed at any temperature less than that. Such was the procedure in the case of copper, gold, silver, and tin. Platinum, however, required a higher annealing temperature than the mica will withstand, so it was wound and annealed on a porcelain tube of the same diameter as the inner tube of the container. Because of its comparatively high resistivity, large enough wire could be used for a 1-ohm coil to be self-supporting, and the annealed platinum coil was readily transferred to the container.

After the coils were annealed, silk or linen thread was wound between turns of the wire. Not only does this insulate adjacent turns, but it holds the coils snugly in place so that there is no tendency for the wire to slip if the containers are turned upside down. This

type of support holds the winding without exerting much pressure against the wire itself. It also holds down the mica so that it does not tend to open outward and press against the wire.

The closed spaces in the containers were filled with air dried with calcium chloride to prevent condensation of moisture when inserted in ice. In the case of the conduits, this was found to be unnecessary. These tubes were closed by packing cotton in the top of the tubes. The small amount of dew that forms evidently spreads over the brass tubes, and the insulation resistance remains sufficiently high. The containers do not remain in ice for a very long time, so little additional moisture diffuses through the cotton.

The first pure-metal standards constructed had 10-ohm coils, and they were mounted in smaller containers than those just described. The wire for these 10-ohm coils, however, was so small that it was difficult to space the turns after they were annealed. The necessary handling of the wire partly offset the advantages of annealing the wire, and the 10-ohm standards have been abandoned.

IV. DETAILS OF RESISTANCE MEASUREMENTS

1. PREPARATION OF THE ICE BATH

Considerable care was taken in the preparation of the ice baths in order to reproduce the temperature accurately. Commercial ice was used, but care was taken to use only the clear part of the ice, avoiding the white core into which the impurities tend to collect. It is believed that such ice is as pure as ice prepared on a small scale from distilled water. One sample of this ice was melted and the water found to have a conductivity of about 3×10^{-6} $\text{ohm}^{-1}-\text{cm}^{-1}$. The ice was carefully shaved and then packed in a thermos bottle. A soft mush was produced by pouring distilled water into the ice. A considerable amount of water was used in order to obtain a good thermal connection between the ice bath and the walls of the resistance standard. Of course, it is necessary to pack in enough of the ice so that it does not float on top of the water.

Apparently the bath is always saturated with air, and water when added is saturated very quickly by air trapped in the finely shaved ice. No change in the temperature obtained was observed when the distilled water was boiled (to drive out the air) and immediately poured into the ice. This rapid saturation probably accounts for the accuracy with which the ice point is reproduced.

Since the ice-point temperature is a function of the pressure, the temperature obtained from the ice bath depends upon the depth of immersion. This change of temperature with depth is about 0.0001° C for 6 inches in depth. As the containers are inserted to the same depth within an inch or two, this variation in temperature is negligible.

2. HEATING BY TEST CURRENT

The inner walls of the containers are made of brass about 0.015 inch (0.375 mm) thick, and as has been stated, the insulation between

it and the coil is mica 0.001 inch (0.025 mm) thick. This construction allows a ready transfer of the heat generated in the coil by the test current. With the test current which was actually used the temperature of the coils was raised about 0.0002° C above the temperature of the ice baths in which they were measured.

3. BRIDGE FOR THE RESISTANCE MEASUREMENTS

The resistance measurements have been made by a substitution method, using a special Thompson double bridge designed and built at this Bureau. With this bridge 1-ohm standards are regularly compared to 1 part in 1,000,000, and a precision of 1 or 2 parts in 10,000,000 is attainable with standards having very low temperature coefficients.

V. DATA ON NEW STANDARDS

Table 1 shows the performance of a number of 1-ohm standards made of pure metal. The resistances given are those which would have been obtained with a negligible test current. These were obtained by making measurements with two different test currents and calculating the value for a negligible test current on the assumption that the increase in resistance of the coils is proportional to the power dissipated in them.

The resistances given in this table are expressed in terms of the Washington unit as maintained at this Bureau since 1910 by means of a group of ten 1-ohm manganin standards. These standards are intercompared every 6 months, and between intercomparisons the pure-metal standards are measured in terms of members of the group of 10. No standard with which the pure-metal coils have been compared has changed more than 1 part in 1,000,000 with reference to the mean, at successive intercomparisons of the reference group.

TABLE 1.—*Data on new standards*

1-OHM STANDARD No. 1

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1931		1932		
Nov. 23	0.999666	Mar. 24	0.999669	Material: No. 22 AWG 0.0253 inch (0.64 mm) commercial copper wire.
Nov. 24	.999666	Apr. 6	.999671	
Nov. 30	.999667	Apr. 25	.999670	Annealing: Annealed Nov. 18, 1931, at 440 C in a large evacuated pyrex tube. About 2 hours were required to raise the temperature to 440 C, after which the heating was cut off. The tube was evacuated by keeping a vacuum pump in continuous operation.
Dec. 7	.999666	Apr. 26	.999670	
Dec. 16	.999666	Apr. 27	.999670	
Dec. 31	.999667	Apr. 28	.999671	
1932		May 3	.999672	
		Aug. 22	.999680	
		Sept. 22	.999683	
Jan. 8	.999669	Oct. 19	.999683	
Jan. 19	.999667	Dec. 22	.999680	
Feb. 11	.999667	1933		
Feb. 16	.999666			
Feb. 29	.999670			
Mar. 8	.999669	May 17	.999680	
Mar. 15	.999669	Oct. 10	.999690	

TABLE 1.—*Data on new standards*—Continued

1-OHM STANDARD No. 2

Date	Resistance at ice point	Date	Resistance at ice point	Notes
1932		1932		
Jan. 19	1.001053	Oct. 19	0.999477	Material: No. 17 AWG 0.045 inch (1.15 mm) commercial tin wire.
Jan. 26	1.000740			
Feb. 11	1.000387	1933		Annealing: annealed for a short time at 200 C in same furnace as standard no. 1.
Mar. 24	1.000185			
May 3	.999537	May 17	.9948	

1-OHM STANDARD No. 3

1932		1932		
Jan. 8	0.998452			Material: No. 22 AWG 0.0253 inch (0.64 mm) commercial "fine" silver wire. As received the wire was very dirty and apparently had not been carefully drawn.
Jan. 19	.998483	Oct. 19	0.998702	
Jan. 26	.998504			
Feb. 11	.998533	1933		
Mar. 24	.998511			
May 3	.998524	May 17	.998707	Annealing: annealed as nearly as possible like standard no. 1.
		Oct. 10	.998913	

1-OHM STANDARD NO. 4

1932		1932		
Jan. 19	0.999475	May 3	0.999427	Material: Same as standard no. 3.
Jan. 26	.999468	Oct. 19	.999411	Annealing: Annealed Jan. 12, 1932, in same way as standard no. 1. At end of this annealing the furnace was found to have been leaking, so furnace was again evacuated and coil raised to 500 C, at which temperature it remained for 1 hour.
Feb. 11	.999480			
Feb. 29	.999453	1933		
Mar. 24	.999427			
		May 17	.999393	
		Oct. 10	.999385	

1-OHM STANDARD NO. 5

1932		1932		
Feb. 11	0.999481	Oct. 19	.999484	Material: Made of 0.048 inch (1.2 mm) commercial platinum wire.
Feb. 16	.999480	Nov. 23	.999484	
Feb. 29	.999480	Dec. 10	.999483	Annealing: Before winding on porcelain mandrel, the wire was heated for a short time in air at about 1,500 C, by passing a current through it. After winding on the mandrel, it was heated in air for 36 hours at about 1,000 C.
Mar. 8	.999481	Dec. 22	.999481	
Mar. 15	.999480			
Mar. 24	.999480	1933		
Apr. 6	.999481			
Apr. 19	.999481	Feb. 11	.999484	
Apr. 25	.999481	Mar. 1	.999483	
Apr. 27	.999481	May 17	.999481	
Apr. 29	.999481	Aug. 2	.999485	
Apr. 30	.999481	Oct. 10	.999483	
May 3	.999481			
Aug. 22	.999482			
Sept. 22	.999484			

1-OHM STANDARD NO. 6

1932		1933		
Feb. 16	0.999816	Feb. 11	.999809	Material: Made of "fine" gold wire 0.0285 inch (0.724 mm) in diameter.
Feb. 29	.999812	Mar. 1	.999809	
Mar. 8	.999813	May 17	.999807	Annealing: Before winding on container tube, the wire was heated in air for a short time at 800 C. After winding on tube, it was annealed just like standard no. 1 except that furnace was heated to 500 C.
Mar. 15	.999809	Aug. 2	.999809	
Mar. 24	.999806	Oct. 10	.999806	
May 3	.999809			
Aug. 22	.999810			
Sept. 22	.999809			
Oct. 19	.999809			
Nov. 23	.999807			
Dec. 21	.999808			

VI. DISCUSSION OF DATA

1. MATERIAL

No analysis has been made of the wires used in the construction of the pure-metal coils. However, some general information has been obtained by measurements of their temperature coefficients of resistance. The average temperature coefficient, per degree C, between 0 and 25 C, in terms of the resistance at 0 C is given by α_0 in table 2.

TABLE 2.—*Temperature coefficients of resistance*

Coil no.	Material	α_0
1	Copper	0.0043
4	Silver	.0040
5	Platinum	.0032
6	Gold	.0032

These temperature coefficients show the copper and silver wires to be of high purity. The platinum and gold coils, however, must contain a considerable amount of impurities as their coefficients are below the values generally accepted for these pure metals.

2. ANNEALING

Coil no. 1 (copper) was annealed at a temperature chosen on the basis of results obtained by Bardwell.[8] He annealed a number of samples of copper wire from the same ingot at different temperatures and then measured their electrical conductivities. He found that the conductivity increased 2 or 3 percent for an annealing temperature of about 350 C. Lower temperatures produced little change in conductivity and higher temperatures gave no appreciable additional change even up to a temperature of about 700 C. Above this temperature the conductivity decreased at an accelerating rate, probably from oxidation, as the material was annealed in air.

In annealing the platinum coil (no. 5), an attempt was made to restore the crystals broken in drawing and winding without producing a larger grain size. For this reason the final annealing temperature was limited to 1,000 C.

No information was found as to the proper annealing temperatures for gold and silver. The temperatures chosen, however, seemed to leave the wire "dead soft." The temperature at which the tin was annealed was probably such as to produce a large grain size. The rapid decrease in the resistance of this coil seems to show that crystal growth is continuing at room temperature.

3. STABILITY

The pure-metal standards have not been under observation for a time long enough to warrant very definite conclusions as to their performance. However, since standards made of alloys change most rapidly in resistance during the first few months after they are completed, it is possible that the pure-metal standards will do the same. Hence, if we can produce pure-metal standards that are very stable when new, they will possibly remain so over long periods of time.

[8] Bardwell, Trans. A.I.M.E., vol. 49, p. 753, 1914.

In considering the stability of these pure-metal resistance standards, it must be kept in mind that there are several possible causes for changes in the value obtained for their resistance. That is to say, changes in the resistance as measured at the ice point may be due to differences in ice-bath temperatures, uncertainties in the electrical measurements, changes in the resistance of the manganin standards with which the pure-metal coils are compared, or actual changes in the resistance of the pure-metal coils themselves. The uncertainty of the electrical measurements is about 1 part in 1,000,000. No relative values, however, may be assigned to the other factors. Over short periods of time it would be expected that fluctuations would be due primarily to changes in ice-bath temperatures while over long periods of time changes in the resistance of the pure metal or the reference coils might be appreciable.

In the period of about 20 months since the last of these coils was completed the copper coil has apparently increased in resistance by about 25 parts in 1,000,000, the gold coil has decreased by about 10 parts in 1,000,000, the platinum coil shows little change, and the performance of the other three coils has been unsatisfactory.

The change in resistance of the gold coil occurred almost entirely during the first month, with no appreciable subsequent change. The major part of the changes in the copper, the silver, and the tin coils occurred during the hot summer months. This has also been observed in the case of sealed manganin coils, which seem to change much more rapidly in resistance during the summer months than during the winter. This is rather surprising as the difference in absolute temperature between summer and winter is not very large, and the fluctuations in temperature are probably as great during the winter months as during the summer.

Except for the change in the gold coil during the first month after its completion, both the gold and the platinum coils have remained very constant in resistance. Their performance should justify the construction of several additional coils of the same materials, in order to see whether or not the pure-metal coils remain constant among themselves. It would seem desirable, moreover, to use materials of higher purity than was obtained for the coils already constructed.

In the spring of 1933, since some of the pure-metal standards had remained very constant in resistance, it was decided to measure the temperature of the ice baths in terms of the triple point of water. A series of 20 measurements was made, extending from March 3, 1933, to May 26, 1933. For this series of measurements nine separate ice baths were used, and the triple-point bath was melted and refrozen each time the ice bath was changed. The mean of the 20 determinations showed the ice baths to have a temperature 0.0097° C below that of the triple point of water. Only one determination differed from the mean by more than 0.0001° C. The complete data, together with a description of the methods of measurement, are given in the paper immediately following this one.

Using this value for the difference in temperature between the ice bath and the triple point the resistance of the platinum coil (no. 5) on October 10, 1933, was 0.999514 Washington unit, while the resistance of the gold coil (no. 6) was 0.999837 Washington unit, each at the triple point of water.

WASHINGTON, October 28, 1933.

U.S. Department of Commerce, Bureau of Standards

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REPRODUCIBILITY OF THE ICE POINT

By James L. Thomas

ABSTRACT

In order to test the ice point as a suitable temperature at which to measure pure-metal resistance standards, an investigation has been made of its reproducibility. The results obtained show that the ice point may be readily reproduced to a few ten thousandths of a degree centigrade. This result was arrived at by intercomparing different ice baths, and by comparing the ice point with the triple point of water.

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I. INTRODUCTION

The temperature of an ice bath is known to depend upon a number of factors, that is to say, the ice point depends upon the kinds and amounts of impurities, both solid and gaseous, present in the ice bath, as well as upon the barometric pressure.

It is the purpose of this paper to present some evidence that the temperature of ice baths, even when prepared from commercial ice, is reproducible to a few ten thousandths of a degree centigrade. This conclusion was arrived at not only by comparing the temperature of ice baths with one another, but also by comparing their temperature with that of the triple point of water.

II. RESISTANCE MEASUREMENTS

In the paper [1] immediately preceding this one is a description of a number of 1-ohm resistance standards made of pure metals, which are measured at the temperature of melting ice. Before they were constructed a preliminary investigation was made of the reproducibility of the temperature of the ice point. For this purpose a 10-ohm copper resistance coil was mounted in a double-walled container and arranged so that its resistance while immersed in an ice bath could be measured with a Thomson double bridge. The resistance of this coil was measured in 6 separate ice baths, the measurements extending over a period of 5 days. During this short period of time the resist-

[1] J. L. Thomas, B.S. Jour. Research, vol. 12, p. 313, 1934.

ance of the copper coil as well as that of the manganin standard with which it was compared probably remained constant. Any variation in the measured resistance was due either to uncertainties of the electrical measurements or to differences in the temperature of the various ice baths. The resistance comparisons were made to 1 part in 1 million and the observed change in resistance was also 1 part in 1 million, corresponding to a temperature change of 0.00025° C at most.

The pure-metal resistance standards described in the paper referred to above, together with the bridge, constitute accurate resistance thermometers. The resistances of two of these standards no. 1 (copper), and no. 5 (platinum), observed and recorded to 1 part in 1 million over a period of about 5 months, from November 1932 to May 1933, may be used for purposes of illustration. Allowing for a slow drift in the resistance of the copper standard, assumed to occur at a uniform rate, these observations may be interpreted as indicating the differences in the temperatures of the ice baths used during that period. When so interpreted, the data indicate that the average difference from the mean was 0.00015° C for observations with standard no. 1, and 0.0001° C for observations with standard no. 2, while the maximum deviation from the mean was 0.0005° C, observed with the copper standard. The entire range in temperature indicated by the platinum coil could be attributed to uncertainties in the electrical measurements, as could part of that indicated by the copper coil. That it is possible to prepare duplicate ice baths for which the indicated temperature difference over periods of a few hours is less than 0.0001° C may be inferred from a statement of Scatchard, Jones, and Prentiss.[2] This, however, gives no comparison between ice baths prepared from different materials at different times. Some information on this point, however, has just been published by White.[3] He used a special design of ice bath, and compared the temperature of one bath with that of another that had been prepared several days previously. The temperatures obtained were usually different, but this difference could be made as small as 0.0001° C by renewing the water in the baths.

III. TRIPLE-POINT MEASUREMENTS

While the preceding results seemed to show that the ice-bath temperatures repeat to a high degree of accuracy, it was desired to determine this temperature by comparing it with the triple point of water. For this purpose a triple-point container was constructed which was very similar to that built by Michels and Coeterier.[4] A cross section of this container is shown in figure 1. The outer wall of the container is of pyrex glass 6 cm in diameter and about 25 cm in length. Into the top of this is sealed a long 1-cm tube with an enlargement at the lower end. This tube is also of pyrex glass. Two heavy-walled tubes are sealed into the sides of the container near the top. These serve both as filling tubes and as supports for the container. The observations made with this container indicate that it would have been more satisfactory if the portion forming the well at O had been of the same diameter as the tube above it.

[2] Jour. Am. Chem. Soc. vol. 54, p. 2688, 1932.
[3] Walter P. White, Jour. Am. Chem. Soc. vol. 56, p. 20, 1934.
[4] Michels and Coeterier, Proc. K. Ak v. Wetensch. Amsterdam, vol. 30, p. 1017, 1927.

The space W between the two tubes was filled about three fourths full with pure water, the air above the surface of the water removed, and the container sealed. The well O was then partly filled with mercury. The water in the space W is partly frozen by immersing the container in a mixture of ice and salt. As the water will undercool, it is necessary to shake the container to start freezing. After the freezing has started, the container is removed from the ice and salt mixture and surrounded with cracked ice.

Since the melting temperature of the cracked ice is about 0.01° C lower than that of the water in W, the freezing of W will now continue at a very slow rate. This leaves the space in O almost completely surrounded with ice and water at the triple point. The space above the tube connecting to O is at the ordinary ice point as the container is completely covered with the cracked ice. By this means the temperature in O is kept close to the temperature of the triple point of water for hours at a time. While this temperature varies slightly with the depth below the water surface, the variation is negligible as it amounts to only a few hundred thousandths of a degree centigrade.

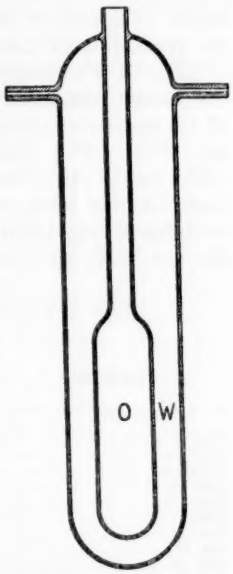

FIGURE 1.—*Container for triple-point bath.*

After being soaked in distilled water for a month the triple-point container was filled in May 1931, evacuated and sealed, and some preliminary determinations were made of the difference in temperature between the triple point and the ice point. The first measurements were made with a special platinum resistance thermometer constructed by C. H. Meyers [5] of this Bureau, used with a Mueller [6] thermometer bridge. Two determinations of the difference between the temperature of an ice bath and the triple point each gave 0.0100C ± 0.0005°C.

In the spring of 1933, since some of the pure-metal standards had remained very constant in resistance, it was decided to measure the temperature of the ice baths to a greater degree of accuracy. The same triple-point container was used, and measurements of the temperature differences were made with the special thermocouple potentiometer designed and built at this Bureau by Brooks and Spinks.[7] This potentiometer was designed to eliminate stray thermal emf's, and any error from this source was undoubtedly less than 0.0001° C. A 50-junction copper-constantan couple was used which had a resistance of about 600 ohms, and the balance was indicated by a specially built galvanometer having an all-copper circuit. This galvanometer was adjusted to be properly damped when connected to the 600-ohm couple, and gave a deflection of about 0.5 mm for an emf of 0.2 microvolt. That is, the temperature difference between the two ends of the couple could be read to 0.0001° C by adjusting the galvanometer balance to 0.5 mm, which was readily done. The wires of the couple passed through a glass tube from the ice bath to the triple-point bath. This glass tube was packed in crushed ice, so

[5] B.S.Jour. Research, vol. 9, p. 807, 1932.
[6] B.S. Scientific Paper No. 288, 1916.
[7] B.S.Jour. Research, vol. 9, p. 781, 1932.

that only the two copper lead wires passed through the temperature gradient between the ice baths and the room.

In measuring the temperature difference between the ice baths and the triple-point bath, it was found that a smaller difference was obtained if the couples were packed in ice and cooled before being inserted in the baths. This suggested that insufficient time had been allowed in the preliminary measurements for equilibrium conditions to be established. By waiting 24 hours the temperature difference obtained was the same whether the couples were pre-cooled or inserted while still at room temperature.

Before it was found necessary to wait 24 hours to make measurements, a series of eight measurements was made in March 1933. In this series four ice baths were used with two separate freezings of the triple-point bath. However, only the measurements which were made at least 24 hours after the couples were inserted in the baths are recorded in the table below.

After it was decided that it was necessary to wait 24 hours to make the measurements, the triple-point container was refilled and a series of 13 measurements was made extending from April 21, 1933 to May 26, 1933. For this series of measurements five separate ice baths were used, and the triple-point bath was melted and refrozen each time the ice bath was changed. The data obtained are given in the accompanying table, Δt denoting the difference in temperature between the ice bath and the triple point, in degrees centigrade.

TABLE 1.—*Comparison of ice bath and triple-point temperatures*

Date 1933	Ice bath number	Δt in °C	Date 1933	Ice bath number	Δt in °C
Mar. 3	1	0.0097	Apr. 29	2	0.0097
Mar. 7	2	.0097	May 1	3	.0098
Mar. 9	3	.0097	May 2	3	.0097
Mar. 11	4	.0099	May 4	3	.0098
Mar. 13	4	.0098	May 16	4	.0096
Mar. 14	4	.0096	May 17	4	.0097
Mar. 15 [1]	4	.0097	May 18	4	.0097
Apr. 21	1	.0097	May 24	5	.0098
Apr. 25	2	.0098	May 26	5	.0098
Apr. 26	2	.0096			
Apr. 28	2	.0097	Average		.0097

[1] After this measurement the triple-point container was emptied and refilled.

The average barometric pressure during these determinations of Δt was close to 75 cm of mercury. The spread in values obtained for Δt was about what would result from changes in barometric pressure, although no correlation between the pressure and temperature was found. The average value of 0.0097° C checks very well with the results reported by other observers, if we assume that the ice baths are always saturated with air. Foote and Leopold [8] state that air saturated ice melts at a temperature 0.0023° C below that of air-free ice, while Moser [9] found that the temperature of the triple point is 0.0074° C above that of melting air-free ice at standard pressure. A combination of their results shows that when the pressure is 76 cm of mercury air-saturated ice melts at a temperature which is 0.0097° C below the triple point.

[8] Foote & Leopold, Amer. Jour. Sci., vol. 11, p. 43, 1926.
[9] Moser, Annalen der Physik, vol. 393, p. 341, 1929.

IV. SUMMARY

In the preceding sections 3 groups of measurement are described in which a total of 34 ice baths was used. In the first two groups of measurements there is an uncertainty due to the electrical measurements amounting to possibly 0.0003° C. In the case of the triple-point measurements this uncertainty is believed to be not over 0.0001° C. If these uncertainties of measurement are borne in mind it is seen that the range of variations in ice-bath temperatures is about what would be expected from the usual changes in barometric pressure. It is entirely possible that, if corrections are applied for barometric pressure, the ice point is reproducible to 0.0001° C.

In order to obtain this accuracy it is, of course, necessary to use reasonable precautions in preparing the ice baths. Only clear parts of ice should be used; they should be rinsed with distilled water before shaving, and should be at all times handled with clean apparatus. It is probably necessary to use the ice baths in rooms where there is no open flame or other source of contaminating gases.

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KINETICS OF REACTION BETWEEN SILVER BROMIDE AND PHOTOGRAPHIC SENSITIZERS

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ABSTRACT

The kinetics of the reactions of silver bromide with sensitizing materials have been studied for comparison with the process of photographic sensitization by the same compounds. Sodium sulphite, reacting with silver bromide to give metallic silver, and allyl thiocarbamide, reacting with it to give silver sulphide, were chosen. The reactions were followed by change in bromide ion concentration. Data on solubility and adsorption were obtained to assist in interpretation of the results. The reaction with allyl thiocarbamide is autocatalytic; under the conditions of the experiments it appears to take place by decomposition of dissolved material at the surface of the silver sulphide. The sulphite reaction is also autocatalytic, and it seems probable, on theoretical grounds, that this is an essential characterist of the sensitization process.

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I. INTRODUCTION

It is now generally conceded that gelatin suitable for making photographic emulsions contains traces of materials which have a specific sensitizing effect. All of those which have been isolated (1)[1] react with silver halides to form silver sulphide, and the numerous compounds which have been patented (2) for use as sensitizers of silver bromide-gelatine emulsions all have this characteristic or else form the analogous silver selenide or telluride. We have recently found (3)

[1] Numbers in parentheses here and throughout the text refer to the references at the end of the paper.

that sodium sulphite is a sensitizer approaching allyl thiocarbamide in effectiveness. The product of its reaction with silver bromide is metallic silver, instead of silver sulphide. While no sensitizers which reduce silver halides to metal have been isolated from gelatin, it is probable that some silver is formed during the normal ripening process.

All these compounds almost certainly function by reacting with the silver halide of the emulsion, since they become effective only after digestion of the emulsion with the sensitizer under conditions favoring reaction between them. The silver sulphide or silver which is formed becomes the material of the sensitivity nuclei on the grains. It has been evident from the first discovery of the sensitizers, however, that the formation of silver sulphide or silver in the emulsion is not a sufficient condition for sensitization. It frequently causes only fog, as when silver sulphide is formed by addition of alkali sulphides (1) or when most reducing agents are used. Sheppard (1) pointed out that the compounds covered by his patents all have the common characteristic of forming molecular compounds with silver halides, and postulated that the silver sulphide must be formed by rearrangement of such compounds in order to act as a sensitivity nucleus. Sodium sulphite falls under this classification, since the well-known solubility of silver halides in a solution of sodium sulphite indicates the formation of a complex silver-sulphite ion.

We have studied the kinetics of the reactions between silver bromide and sensitizers with the two-fold purpose of correlating the results with the photographic data and of attempting to find whether a particular reaction mechanism is common to sensitizers. Experiments on this subject have been suspended for lack of funds with the investigation incomplete, but the results which have been obtained are sufficiently promising to warrant publication.

Two sensitizers have been used: sodium sulphite and allyl thiocarbamide. The experiments were carried on under conditions approaching those existing in the emulsion, using a large excess of silver bromide and a low concentration of sensitizer. The progress of the reaction was followed, in both cases, by the change in bromide-ion concentration of the solution. This was determined by the silver-silver bromide electrode, using the apparatus described in a previous communication (4). The method is rapid, convenient, and sensitive. The relative values of bromide-ion activity obtained during a run were correct to about 1 percent, this sensitivity being practically independent of the concentration. The presence of solvents for silver bromide, such as sodium sulphite, allyl thiocarbamide, or ammonia, does not interfere with the working of the electrode provided the solution is saturated with silver bromide. The least unsaturation causes serious error, but the conditions of the reactions, with a large amount of finely divided silver bromide in suspension, insured saturation, and it was found that the electrode responded rapidly enough to give reliable readings even during the progress of the reaction.

II. THE REACTION OF SILVER BROMIDE WITH SODIUM SULPHITE

Sodium sulphite apparently reacts with silver bromide according to the equation

$$2AgBr + Na_2SO_3 + H_2O = 2Ag + 2NaBr + H_2SO_4$$

The solid reaction product is silver, and contains no silver sulphide. All experiments were carried out with exclusion of oxygen by passing a current of nitrogen or hydrogen through the solution.[2] The apparatus was provided with three-way cocks on the inlet and outlet tubes so that sulphite could be introduced and samples removed without admitting air. Samples were caught in thin-walled weighing bottles packed in ice, and rapidly chilled to 30 C, the temperature of the thermostat used for electrode readings of bromide-ion concentrations; at this temperature the rate of reaction was negligible. All reactions were run in the dark room under a Wratten no. 0 safelight, although this precaution was apparently unnecessary.

The first series of reactions was run at $73.4 \pm 0.2°$ C, in unbuffered solutions. All the suspensions contained 0.03 mol AgBr per liter, either without protection or in 1 percent gelatin or 2 percent gum-arabic solution. When unprotected silver bromide was used, it was precipitated and washed just before the reaction. The fresh material was considerably peptized by the sulphite, in the absence of other electrolytes. The results of this series are summarized in table 1. All the reactions were characterized by an induction period, followed by a constant rate of reaction. This constant rate persisted up to a bromide-ion concentration of about 6×10^{-4} N. The rate of reaction decreased slowly after this in the gelatin suspensions and more rapidly in the unprotected ones. The maximum rate given in the sixth column of the table was characteristic of the reaction over most of the period of a 6-hour run and has accordingly been given as the best measure of the reaction velocity. These rates of reaction are of the right order of magnitude to agree with the analytical data (3, figs. 5 and 6) on the extent of the reaction of sulphite with silver bromide during sensitizing.

Unless the constant rate is entirely the result of compensation changes, which is rather improbable for the range of conditions used, it indicates that the rate is relatively independent of bromide-ion concentration when the latter is low enough. The experiments in which bromide was added to the reaction mixture before the start of the reaction confirm this. Inspection of table 1 shows that in reactions with unprotected silver bromide and 0.010 N Na_2SO_3, the maximum rate was 0.48 for an initial $[Br^-]$ 7×10^{-7} and 0.57 for an initial $[Br^-]$ 7.7×10^{-5}. In the presence of gelatin, with the same sulphite concentration, an increase in initial $[Br^-]$ from 4×10^{-6} to 3.8×10^{-4} decreased the rate only from 0.19 to 0.10. At 10^{-3} N, however, reaction was practically stopped. This agrees with the photographic evidence (3), that ripening was very slow even at 65 C pH 7.3 and 0.15 N Na_2SO_3 when the bromide-ion concentration was 5.6×10^{-3} N.

[2] A sulphite solution held in the apparatus for 4½ hours under the conditions of a reaction decreased in titre from 0.00095 to 0.00090 N in that time, indicating that the protection from air was adequate. A suspension of silver bromide in the (deactivated) gelatin was held under hydrogen at 73.40 C for 5½ hours; the reaction in the absence of sulphite increased the bromide-ion concentration only from 2.0×10^{-5} to 3.4×10^{-5} N.

The rate of reaction increased less rapidly than the concentration of sulphite, which is in agreement with the photographic results (3, figs. 4, 5, 6). The data on the effect of hydrogen-ion concentration are approximate only, but indicate that it was of the same order as its effect on photographic sensitization by sulphite (3, fig. 8). This is less than for after-ripening with active gelatin (5) and much less than for the thiocarbamide reaction (next section).

TABLE 1.—*Reaction of sodium sulphite with silver bromide at 73.4 C*

[The induction period is the time required to reach the maximum reaction rate]

Na_2SO_3 concn. N	Colloid	pH	[Br] $\times 10^6$ at start	Induction period	Maximum rate, milli-equivalents Br^- formed per hour per liter	Remarks
				Hours		
0.0102	None	9.0	0.007	¼	0.38	
.0102	do	9.0	.007	¼	.48	
.0105	do	9.0	.004	¼	.47	Exposed to light.
.00089	do	8.7	.006	¼	.15	
.0103	do	9.0	.77	¼	.57	
.0102	do	9.0	9.4	>2	.0	
.0112	Gum arabic	8.5+	0.24	¼	.24	
.0103	Gelatin	8.5	0.024	1½	.17	
.0105	do	7.8	.037	1¼	.17	pH determined at end of reaction.
.0101	do		.045	¾	.20	Made with different gelatin from others; portions of same emulsion; second portion exposed to light.
.0098	do		.040	¾	.18	
.0030	do	8.0	.034	1½	.091	
.0012	do	8.4	.31	1½	.031	Emulsion incompletely washed.
.0101	do	6.8	.12	1¾	.13	pH determined at end of reaction.
.0102	do	6.2	.06	1½	.11	Do.
.0099	do	8.6	3.8	2¼	.10	

The induction period of the reaction was lengthened by protective colloids. Gum arabic was less effective than half the amount of gelatin, which is in accordance with their relative ratings as protective colloids. At 73.4 C the colloids appeared to decrease the maximum rate of reaction; the reaction mixtures with and without colloids unfortunately were not otherwise identical, but the differences in bromide and hydrogen-ion concentrations do not appear sufficient to explain the differences in rate.

The existence of the induction period indicates that the reaction is autocatalytic, and therefore presumably takes place at the surface of the new solid phase. It should, then, be accelerated by adding silver. The data of table 1 show that exposure of the silver bromide to light was not sufficient to accelerate the reaction. A new series [3] of experiments were made with special reference to the autocatalysis. The temperature was raised to 88.2 C so that the reactions could be carried nearer completion in the time available for each run. The reaction mixtures were buffered to pH 6.7 with $N/2$ sodium acetate-acetic acid mixture (see table 2) to simplify the kinetics by minimizing the change in pH during the reaction; this, however, tended to coagulate the silver bromide. The data were less regular, probably for this reason.

[3] The first series was intended as a preliminary survey, which would be continued after obtaining comparative results with allyl thiocarbamide. This became impossible so the second series was limited as indicated.

TABLE 2.—*Buffer solutions used for reaction mixtures of allyl thiocarbamide and silver bromide*

[410 ml water and 62.5 ml of 4 *M* sodium acetate, to which was added 0.050 *N* acetic acid, as follows. pH determined with hydrogen electrode at 30.0 C]

Ml HAc solution	5.0	10.0	15.0	23.0	27.5	40.0	60.0
pH	7.64	7.29	7.11	6.92	6.84	6.67	6.48

The tenth-normal sodium acetate buffer contained 5.0 ml of 0.050 *N* HAc and 12.5 ml 4 *M* NaAc in 500 ml; pH 6.77.

Figure 1 represents the results of these experiments. Curves 1 and 4 show the typical course of the reaction without catalyst. In

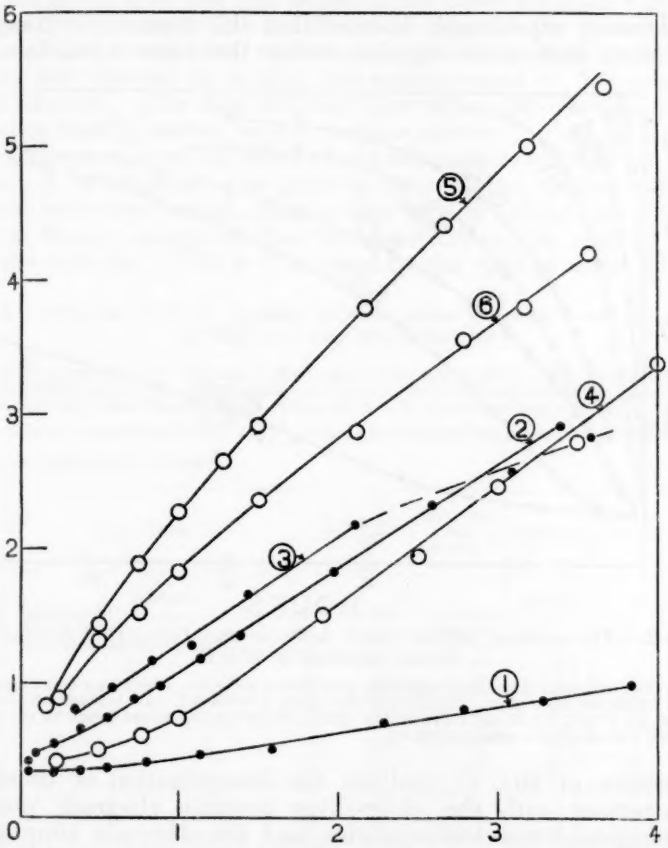

FIGURE 1.—*Rate of reaction between silver bromide and sodium sulphite solutions at 88.2 C.*

Abscissas, time in hours; ordinates, bromide-ion concentration of solution, $\times 10^4$. Curves 1, 2, and 3 for 0.0012 *N* Na_2SO_3, curves 4, 5, and 6 for 0.0033 *N* Na_2SO_3. Curves 1 and 4, silver bromide suspended in 1 percent gelatin. Curves 2 and 5, silver bromide plus silver, suspended in 1 percent gelatin. Curves 3 and 6, silver bromide plus silver, without protective colloid.

the other experiments, colloidal silver was added before the sulphite. It was prepared by allowing the silver bromide to react with sodium sulphite, then washing thoroughly by decantation before using it for the kinetic experiment.[4] Approximately one half milli-equivalent

[4] The product was a brown absorption compound, from which the silver could not be removed completely by nitric acid.

of metallic silver was added to one half liter of reaction mixture. The curves show clearly that the induction period was completely eliminated by the addition of the silver. The order of the reaction remained less than one. As in the other series, the rate began to decrease irregularly in the unprotected mixtures after a relatively short interval. In the presence of sufficient silver, the maximum rate was apparently the same with and without gelatin.

III. THE REACTION OF SILVER BROMIDE WITH ALLYL THIOCARBAMIDE

1. EXPERIMENTAL METHODS

Preliminary experiments showed that this reaction is many times faster than that with sulphite under the same conditions. The

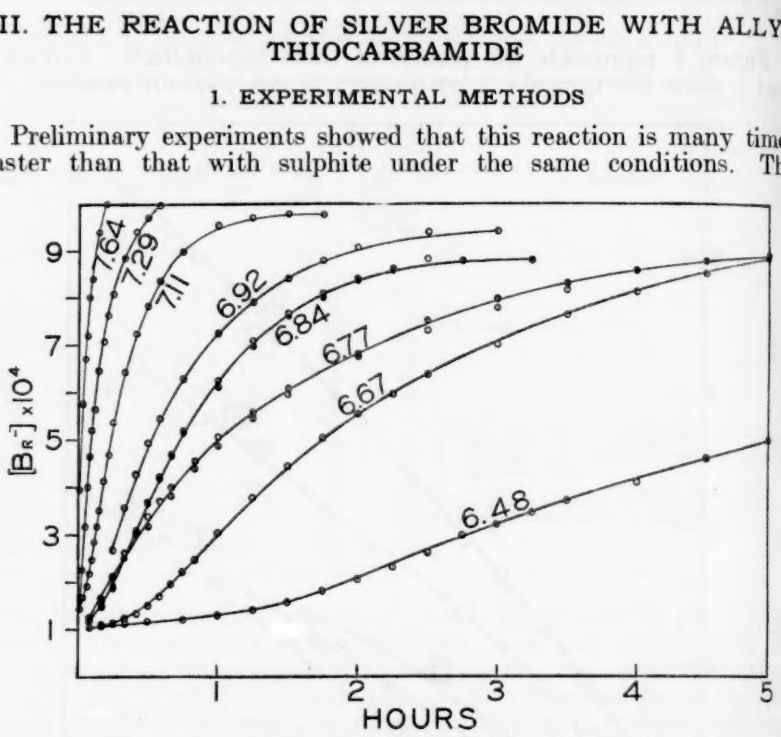

FIGURE 2.—*The reaction between silver bromide and 1.00×10⁻³ N allyl thiocarbamide solutions at 30.0 C.*

Abscissas, time from start of reaction; ordinates, bromide-ion activities, which are a direct measure of the reaction which has taken place. Numbers on the curves give the pH. All buffered with NaAc–HAc mixtures; 0.1 *N* for pH 6.77 and 0.5 *N* for the others. No protective colloid except for the runs at pH 6.84 which were made in a gelatin emulsion.

temperature of 30.0 C used for the determination of bromide-ion concentrations with the silver-silver bromide electrode proved to give convenient reaction velocities, and the electrode adapted itself so rapidly to the solution that it was found possible to run the reactions in the air thermostat used for the electrode measurements, the silver electrode and salt bridge being left in place throughout the reaction. This arrangement had the great advantage that readings could be taken almost continuously when needed.

The electrode was coated with silver sulphide at the end of a run, but continued to give normal readings in known bromide solutions. In the few cases where the electrode gave trouble it was quite obvious from the erratic nature of the potential. The window of the thermostat was coated with orange lacquer which excluded practically all

light of less than 500m μ wave length, but as a further precaution a black curtain was kept over it. The silver bromide was necessarily exposed to light in setting up the apparatus, but the results with sulphite indicate that this was not likely to affect the reaction.

As this reaction was known in advance to be sensitive to hydrogen-ion concentration, all the reaction mixtures were buffered. Tenth normal ammonium acetate was used in some of the runs; the pH was 6.68 at first, falling to about 6.5 on completing reaction with 0.001 *N* allyl thiocarbamide. Acetic acid-sodium acetate mixtures were adopted later; compositions of the mixtures and pH determined at 30.0 C with the hydrogen electrode are given in table 2. In using these, the acetic acid was first added to the silver bromide suspension, then the thiocarbamide; no reaction took place in the presence of the acetic acid and the mixture could be brought to equilibrium before the reaction was started by adding the concentrated (4 *M*) solution of sodium acetate. The final addition took about 60 seconds, the mixture being rapidly stirred with a turbine stirrer.

The original data on the effect of pH on reaction velocity are plotted in figure 2 to illustrate the general form of the curves. After an extended induction period, the reaction usually follows the first order equation closely enough so that the constant can be used to characterize the velocity. This is illustrated by the data given in table 3.

TABLE 3.—*Original data of reaction between silver bromide (with no protective colloid) and allyl thiocarbamide*

[0.03 mol AgBr suspended in 477 ml water at 30.0 C, plus 5.0 ml 0.050 *N* HAc. Then added 5.0 ml 0.100 *N*[1] allyl thiocarbamide solution and allowed mixture to reach equilibrium with electrode. Reaction started by adding 12.5 ml of 4.0 *M* NaAc solution, raising pH to 6.77; time taken from this. Velocity constants calculated from the equation $K=\frac{2.303}{t}\log\frac{a}{a-x}$ where a is the initial concentration of allyl thiocarbamide and x is the concentration at time t]

Time	emf of cell	Bromide-ion activity *N*	Reaction	$k\times10^3$
Minutes			*Percent*	
Before addition.....atc	−0.0968	1.08×10^{-6}	.....	.....
After addition.....atc	+.0125	7.09×10^{-3}	.....	.....
After addition NaAc.....0	.0221	1.02×10^{-4}	0.	.....
5	.0258	1.18×10^{-4}	2.1	4.
10	.0345	1.65×10^{-4}	8.1	8.7
15	.0411	2.12×10^{-4}	14.3	10.4
20	.0467	2.63×10^{-4}	20.8	11.7
25	.0502	3.01×10^{-4}	25.8	12.0
30	.0533	3.38×10^{-4}	30.6	12.2
35	.0557	3.71×10^{-4}	34.9	12.2
40	.0577	4.00×10^{-4}	38.7	12.2
50	.0611	4.56×10^{-4}	45.9	12.3
60	.0638	5.06×10^{-4}	52.2	12.3
75	.0664	5.59×10^{-4}	59.0	11.9
90	.0686	6.08×10^{-4}	65.5	11.9
120	.0713	6.75×10^{-4}	74.1	11.3
150	.0734	7.31×10^{-4}	81.3	11.3
180	.0750	7.80×10^{-4}	87.9	11.8

[1] Concentrations of allyl thiocarbamide have been expressed in terms of normality with respect to silver. Thus, 0.10 N=0.05 M. This does not affect the velocity constant, but comes into the equilibrium equations.

Independent evidence of the influence of some of the variables was obtained by a different method of following the reaction. In these experiments the bromide-ion activity was held constant by addition of 0.0100 *N* silver nitrate solution and the rate of reaction measured by the necessary rate of addition of the silver. A turbine stirrer

operated as rapidly as possible without splashing was used to mix the silver solution with the suspension. If the flow of solution was temporarily interrupted it was very evident from the rate of change of electrode potential that the rate of reaction with the silver bromide corresponded to the rate of addition of solution which had been required. These experiments gave particularly clear evidence of the autocatalytic nature of the reaction. For example, the data of curve 4, figure 3, were plotted on a large scale and the slope of the curve, giving the instantaneous rate of reaction, carefully measured at each

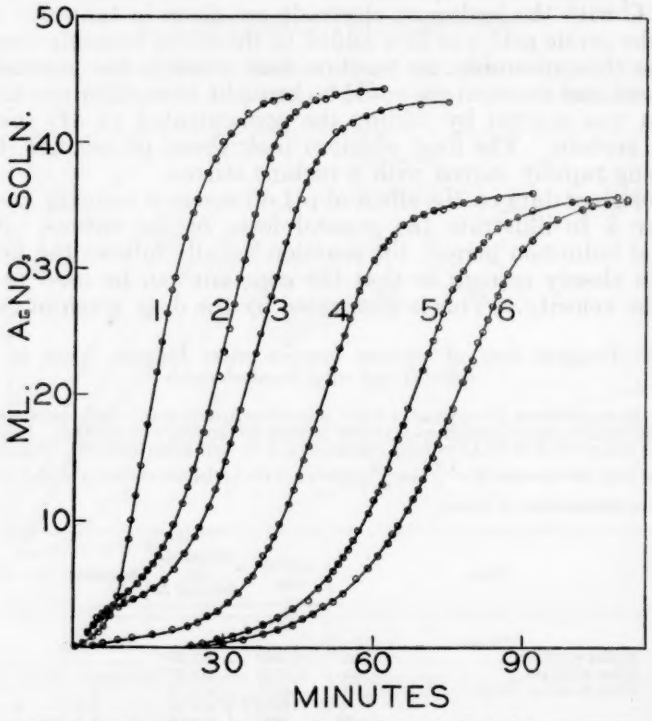

FIGURE 3.—*The reaction between silver bromide and allyl thiocarbamide at 30.0 C and constant bromide-ion concentration.*

pH maintained at 6.84 by 0.5 *N* NaAc—HAc buffer. Conditions for the runs are given under the corresponding numbers in table 5. As all those illustrated were made with 0.5 liter of 1.00×10^{-3} *N* allyl thiocarbamide, 50 ml of the $AgNO_3$ solution would represent complete reaction.

ml addition. Up to 10 ml, 20 percent reaction, the rate of reaction was proportional within 5 percent to the percentage reaction, after which it rapidly approached a constant value.

The results of this series were obviously not as reproducible as the others; they were probably much more dependent on mechanical details such as the mixing of the solution. It will be noted, however, from table 5 that the maximum rate of reaction and the fraction of the total occupied by the induction period were reasonably constant for given conditions; the greatest variation was in the time of the induction period which appears to be less significant. It will also be noted that these reactions did not run to completion like the others, and that the reactions in the emulsion were the least complete.

2. VARIABLES AFFECTING THE RATE OF REACTION

The curves shown in figure 3 indicate that the reaction is autocatalytic. It was readily demonstrated that silver sulphide is the catalyst. The mixture of silver bromide and silver sulphide left from a previous reaction was thoroughly washed and used to make up the suspension for a new experiment, the conditions otherwise being the same as those given in table 3. The reaction between the allyl thiocarbamide and the silver bromide-silver sulphide mixture started at the maximum rate (3 percent per minute) with no induction period, and followed approximately the equation

$$\frac{d[Br]}{dt} = k.\frac{a-x}{[Br^-]}$$

In another experiment, colloidal silver sulphide was prepared by decomposition of sodium thiosulphate in the presence of gelatin. This was added to a Lippmann emulsion which had previously been found to react with allyl thiocarbamide in the absence of catalyst only after a long induction period. With the addition of the colloidal silver sulphide, there was no induction period and the reaction was even more rapid than in the previous experiment with unprotected silver bromide-silver sulphide mixture. It should be noted that in this second case it is very improbable that the silver bromide and silver sulphide were in contact. Silver bromide carrying colloidal silver from a previous reaction with sodium sulphite reacted at a normal rate with allyl thiocarbamide, indicating that the catalysis by silver sulphide is specific.

Calculation from the data given in figure 2 indicates that the rate of reaction varies inversely as the square of the hydrogen-ion concentration, as a first approximation. Velocity constants could not be calculated for the more rapid reactions, so the slopes of the curves at $[Br^-]$ 3.5×10^{-4} were taken as the rate for this estimate. At pH 4.7 no reaction can be detected for several hours; the practical limit lies about at Sheppard's original figure of pH 6. The effect of acid on the reaction is therefore even greater than on after-ripening with active gelatin (5). After-ripening is quite appreciable at pH 5, which indicates the presence of sensitizers other than allyl thiocarbamide in gelatin.

The reaction velocity varied approximately as $\frac{1}{[Br^-]^{1/2}}$.

This relation may be obtained either from the maximum velocities of the reaction at constant $[Br^-]$, or from the constants of table 4. This is much greater than the effect of bromide-ion concentration on photographic after-ripening (6).

The last three experiments listed in table 5 indicate that the rate of reaction is directly proportional to the concentration of allyl thiocarbamide, the maximum rates corresponding to about the same percentage of the original concentration in each case. The run with 3×10^{-3} N allyl thiocarbamide, corrected for the increased bromide-ion concentration, comes within 20 percent of the same ratio.

TABLE 4.—*Velocity of reactions of silver bromide with allyl thiocarbamide, buffered by 0.10 N ammonium acetate, without protective colloid, at 30.0 C.*

[0.03 mol silver bromide per liter of reaction mixture. Initial pH 6.68]

Initial concentration of allyl thiocarbamide N	Initial bromide-ion activity N	$k\times10^3$	Initial concentration of allyl thiocarbamide N	Initial bromide-ion activity N	$k\times10^3$
3.00×10^{-4}	6.5×10^{-5}	20.1	1.00×10^{-3}	1.66×10^{-4}	6.4
1.00×10^{-3}	9.7×10^{-5}	9.6	1.00×10^{-3}	1.6×10^{-4}	6.3
1.00×10^{-3}	9.6×10^{-5}	10.5	1.00×10^{-3}	2.4×10^{-4}	2.25
1.00×10^{-3}	9.6×10^{-5}	11.3	1.00×10^{-3}	3.1×10^{-4}	1.57
3.00×10^{-3}	2.7×10^{-4}	1.41	1.00×10^{-3}	3.4×10^{-4}	1.6

TABLE 5.—*Reaction velocities at constant bromide-ion concentration*

[All experiments at 30.0 C, pH 6.84 (0.5 N HAc−NaAc buffer), 0.03 g equivalent of silver bromide per liter of reaction mixture]

Curve number in fig. 3	[Br⁻]	Allyl thiocarbamide concentration N	Maximum velocity milliequivalents per hour per liter	Induction period		Remarks
				Percent of reaction	Minutes	
1	3.1×10^{-4}	1.00×10^{-3}	2.8	10	9½	No protective colloid.
	2.4×10^{-4}	1.02×10^{-3}	7.7	30	12½	Do.
2	3.1×10^{-4}	1.00×10^{-3}	2.05	28	24	Silver bromide precipitated and washed before suspending in gelatin.
3	3.1×10^{-4}	1.00×10^{-3}	1.75	30	30	
	3.1×10^{-4}	1.00×10^{-3}	3.0	35	29	Emulsion made by adding silver nitrate solution rapidly in small portions.
	3.1×10^{-4}	1.00×10^{-3}	1.75	40	40	
	3.1×10^{-4}	1.00×10^{-3}	.02	.....	>1,000	Lippman type ("grainless") emulsion.
4	3.1×10^{-4}	1.00×10^{-3}	1.45	24	35	
5	3.1×10^{-4}	1.00×10^{-3}	1.35	26	50	Emulsion, made by adding silver nitrate solution in continuous fine stream for 10 minutes.
6	3.1×10^{-4}	1.00×10^{-3}	1.15	27	70	
	1.2×10^{-4}	1.00×10^{-3}	5.5	35	12	
	3.6×10^{-4}	3.00×10^{-3}	2.6	23	45	
	2.6×10^{-4}	0.51×10^{-3}	0.98	40	36	Emulsion made by adding silver nitrate in continuous fine stream.
	2.5×10^{-4}	1.02×10^{-3}	1.93	30	40	
	3.0×10^{-4}	2.04×10^{-3}	3.36	30	54	

The rates of reaction for the experiments listed in table 4 have been characterized by the "constants" obtained from the first order equation, as in table 3. These were found to be dependent on the initial bromide-ion concentration; it will be noted that the constant was practically the same for an initial $[Br^-]$ of 3×10^{-3} in the cases where this represented simply the solubility of AgBr in 3×10^{-3} N thiocarbamide, and where the reaction mixture contained 1×10^{-3} N thiocarbamide plus soluble bromide.

The apparent first order of the reaction was obviously the result of compensation between the autocatalysis and the factors decreasing the rate of reaction. The rate of reaction during the period of autocatalysis may possibly be expressed by thus:

$$-\frac{dx}{dt}=k\frac{(a-x).x}{[Br^-]^n},$$

the x in the numerator corresponding to the autocatalytic factor. If n is close to 1, and $[Br^-]$ is proportional to x, as in reactions starting

with pure silver bromide and allyl thiocarbamide, this reduces to a pseudo first order. If soluble bromide had been added to the reaction mixture before starting, [Br^-] was no longer proportional to x and it was observed that the first-order equation fitted less closely.

An unexpected and important feature of the data was that the reaction velocity proved to be independent of the amount of silver bromide present. Ordinarily the silver bromide was equivalent to nearly 30 times the allyl thiocarbamide. When this ratio was reduced to 2.6, the results of a run without gelatin, buffered with ammonium acetate, checked the previous data within the limit of reproducibility. The experiment was repeated using an "emulsion" of silver bromide in gelatin. The excess in one case was reduced to 5 percent, gelatin being added to keep the concentration 1 percent both in this run and in the control with 2,600 percent excess AgBr. The difference between the two was so small as to be doubtful.

The effect of gelatin is not as large in this reaction as in the one with sulphite. It is most evident as an increase in the induction period. In the extreme case of the "grainless" emulsion recorded in table 5 there was no measurable reaction in 15 hours. Another very fine-grained emulsion required 30 minutes to react as much as a normal emulsion in 5 minutes under the same conditions; once under way, the "constants" were about the same as in the normal emulsion.[4] The curve for pH 6.84 in figure 2 was obtained with gelatin emulsions, and falls in well with the others which were made with unprotected silver bromide, although there is a possible difference in induction period. The effect of the gelatin on induction period is also evident in the curves for reaction at constant [Br^-], figure 3; here there is also a definite effect on the rate of reaction after the induction period.

IV. ADSORPTION AND SOLUBILITY DATA

1. ADSORPTION OF POTASSIUM BROMIDE TO SILVER BROMIDE

Silver bromide was known to adsorb soluble bromides, but no quantitative data were available for the region involved in these reactions. They were obtained by the use of the electrode, the bromide-ion concentration in suspensions of silver bromide being determined after successive additions of potassium bromide solution. The silver bromide used for the experiments was precipitated at room temperature from 0.5 N solutions of silver nitrate and potassium bromide, the latter being 10 percent in excess to prevent precipitation of the trace of chloride which persists through repeated recrystallization of the bromide. The precipitate was washed with 15 portions of hot distilled water; its suspension before adding soluble bromide gave a bromide-ion concentration within ± 5 percent of the value calculated from the solubility product of silver bromide at 30 C. The data are presented graphically in figure 4 as g mols of KBr per g mol of AgBr; this ratio may be converted to the weight basis by multiplying by 0.58.

[4] It was not possible to determine whether a "grainless" emulsion would react normally with sulphite, as a highly transparent washed emulsion of this type became opaque after a few minutes at 88 C, indicating a coagulation.

2. SOLUBILITY OF SILVER BROMIDE IN SODIUM SULPHITE SOLUTIONS

The solubility of the silver bromide in the sodium sulphite solutions at 30.0 C could be estimated from the original electrode readings in the reaction mixtures, since the bromide-ion concentration (corrected for the solubility of silver bromide in pure water) was equal to the dissolved silver bromide. In 0.010 N Na_2SO_3 (pH 8.5) the silver bromide was $7.5 \pm 0.5 \times 10^{-5}$ N; this was reduced to 3.5×10^{-5} N in a gelatin emulsion at pH 6.2 with the same sulphite concentration, and to 4×10^{-5} N by the addition of 4×10^{-4} N KBr at pH 8.5. The solubility in 0.0030 N Na_2SO_3 was 2.9×10^{-5}, and in 0.0012 N, 2.0×10^{-5}. These figures are about double the values of Mees and Piper (7) obtained by analysis at room temperature. At the reaction temperatures the solubility was probably several times as great, but

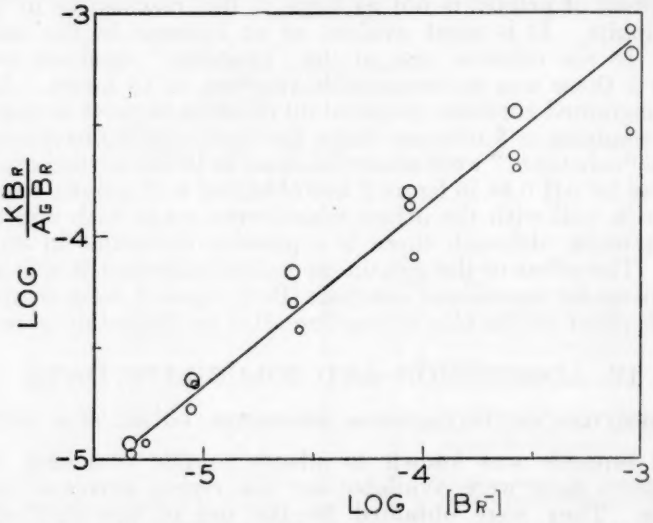

FIGURE 4.—*Adsorption of KBr by AgBr, in the absence of gelatin, at 30.0 C. The different size circles indicate separate series of measurements.*

the variation with concentration of sulphite, and hydrogen and bromide ions may be expected to be parallel to the results at lower temperature.

No data on the adsorption of sulphite to silver bromide were obtained.

3. SOLUBILITY OF SILVER BROMIDE IN ALLYL THIOCARBAMIDE SOLUTIONS

The available data on the solubility of silver bromide in allyl thiocarbamide solutions do not cover the range of concentrations used in our experiments or the equilibrium relations. Pawelka (8) measured the equilibrium between silver ion and thiocarbamide electrometrically and found that the complex ion consisted of three molecules of the latter to one silver ion. The data of table 6 indicates that when there is a sufficient excess of allyl thiocarbamide over silver, the complex ion is $Ag(atc)_2^+$, but that as the concentration of silver is increased more and more of the 1 : 1 ion is formed.

In dilute solutions of allyl thiocarbamide saturated with silver bromide the thiocarbamide-silver ratio is such that the 1:2 ion is still the principal form. When silver bromide goes into solution in a solution of allyl thiocarbamide, bromide ions and complex silver-thiocarbamide ions must be formed in equal numbers. Their normalities will therefore be equal, provided the solubility of silver bromide in pure water may be neglected. The concentration of dissolved silver bromide may thus be determined simply by electrometric measurement of $[Br^-]$ in the solution.

TABLE 6.—*Equilibrium in allyl thiocarbamide. silver-nitrate mixtures at 30.0 C, pH 3.34*

[Constants calculated from the equation $K=\frac{[Ag^+]\times[atc]^2}{[Ag(atc)_2^+}$]

$AgNO_3$, N	Allyl thiocarbamide N	$[Ag^+]$	K
2.71×10^{-5}	2.17×10^{-3}	2.47×10^{-12}	4.24×10^{-11}
5.42×10^{-5}	2.16×10^{-2}	4.68×10^{-12}	4.00×10^{-11}
1.07×10^{-4}	2.15×10^{-2}	9.71×10^{-12}	4.15×10^{-11}
2.13×10^{-4}	2.13×10^{-3}	2.10×10^{-11}	4.32×10^{-11}
4.17×10^{-4}	2.08×10^{-2}	5.49×10^{-11}	5.25×10^{-11}
8.00×10^{-4}	2.00×10^{-2}	1.21×10^{-10}	5.10×10^{-11}
1.48×10^{-3}	1.85×10^{-2}	4.50×10^{-10}	7.20×10^{-11}
1.86×10^{-3}	1.77×10^{-2}	9.40×10^{-10}	9.9×10^{-11}
2.21×10^{-3}	1.70×10^{-2}	2.00×10^{-9}	14.2×10^{-11}
2.52×10^{-3}	1.63×10^{-2}	4.02×10^{-9}	20.2×10^{-11}

Under conditions where only a single species of complex ion is formed, the solubility relations are quite simple. We have, first, that

$$[Ag(atc)_2^+]=[Br^-]. \tag{1}$$

Since

$$[Ag^+]\times[Br^-]=S_{AgBr}, \tag{2}$$

we may make the substitutions

$$\frac{[Ag^+]\times[atc]^2}{[Ag(atc)_2^+]}=K=\frac{S\times[atc]^2}{[Br^-]\times[Ag(atc)_2^+]} \tag{3}$$

$$\frac{[atc]^2}{[Ag(atc)_2^+]}=\frac{K}{S} \text{ or } \frac{[atc]}{Ag(atc)_2^+}=K^1 \tag{4}$$

Thus the ratio of free allyl thiocarbamide to the complex ion is a constant and, as a first approximation, the solubility of silver bromide is directly proportional to the total concentration of allyl thiocarbamide. Figure 5 shows how well this relation holds for the range of concentrations used in the velocity experiments. At pH 3.3 (0.005 N HAc), the solutions were quite stable, so that the equilibrium measurements could be made without difficulty. The upper limit at which solubility could be measured was about pH 6.8, and the data in figure 5 at pH 6.49 and the lower concentrations are possibly in error from reaction in the solution. As already mentioned, the more concentrated solutions are the slower to react because of their higher bromide ion concentration.

The solubility increased rapidly with pH. K in equation 3 fell from 15.4×10^{-11} at pH 3.34 to 3.0×10^{-11} at pH 6.77. Assuming that

the formation of the complex ion is dependent on the presence of free amino groups in the allyl thiocarbamide, this is evidence for the "zwitterion" theory of its structure.

In mixtures of allyl thiocarbamide and soluble bromide, equation 3 should hold, but not equation 4. Mixtures of allyl thiocarbamide and soluble bromide, in buffer solution at pH 6.77, were made up and saturated with silver bromide. It was found that the solubility was roughly proportional to the thiocarbamide concentration, in spite of the addition of soluble bromide. (The measurements of solubility in this case were less accurate, since the solutions were unstable and the increase in [Br^-] on adding the AgBr was small.) Since part of

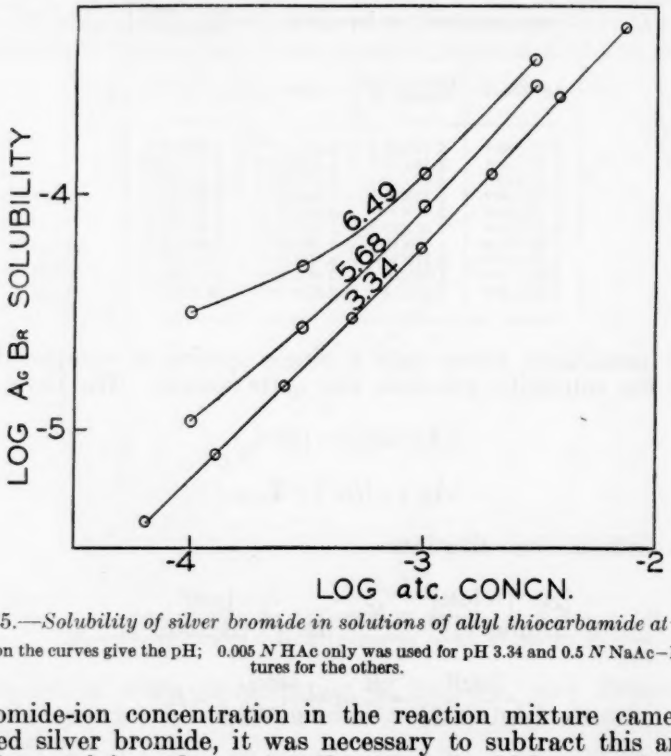

FIGURE 5.—*Solubility of silver bromide in solutions of allyl thiocarbamide at 30.0 C.*

Numbers on the curves give the pH; 0.005 *N* HAc only was used for pH 3.34 and 0.5 *N* NaAc−HAc mixtures for the others.

the bromide-ion concentration in the reaction mixture came from dissolved silver bromide, it was necessary to subtract this amount from the total in order to get the amount which came from the product of the reaction; the amount subtracted being under 10 percent, an approximate correction was satisfactory.

A few experiments were completed on the adsorption of allyl thiocarbamide on silver bromide. The thiocarbamide solutions (in 1.0×10^{-4} *N* H_2SO_4, pH 4.7) were stirred with silver bromide prepared as for the experiments on adsorption of soluble bromide, and the change in concentration determined. The conditions chosen were not satisfactory, but in 5.0×10^{-4} *M* allyl thiocarbamide (1.00×10^{-3} *N*), 1×10^{-3} mol was adsorbed on 1 mol of AgBr; at 2.9×10^{-4} *M*, the adsorption per mol AgBr was 4×10^{-4}. These values are approximately double the corresponding ratios for *K*Br on AgBr.

V. DISCUSSION

To the best of our knowledge the only other studies of the kinetics of reactions in which a solid phase reacts with a solution to form a new solid phase have also been in connection with a photographic problem, that of development (9). Our experimental methods show promise of being applicable to development as well as to sensitizer reactions.

Complete mathematical analysis of the kinetics of the reactions which we have studied would be extremely difficult in any case, but even with the limited data available it is possible to draw a few definite conclusions. The reaction with allyl thiocarbamide will be considered first because more information is available. Under the conditions of our experiments the first step must have been the formation of the complex ion in solution. It could not have proceeded by adsorption of allyl thiocarbamide to silver bromide followed by a slower rearrangement of the adsorption complex, since the rate was practically independent of the amount of silver bromide. Furthermore, colloidal silver sulphide, added separately from the silver bromide under conditions which preclude its adsorption by the latter, catalyzed the reaction so strongly that it evidently takes place at the silver sulphide surface and is not restricted to the silver sulphide-silver bromide interface. These statements are for the conditions of our experiments, and do not necessarily apply to conditions in the emulsion with a much lower concentration of allyl thiocarbamide. In the emulsion, the ratio of adsorbed sensitizer to sensitizer in solution is probably greater than one; in our experiments it was less than one. However, it seems probable that the reactivity of the material in solution is considerably greater than that of the material adsorbed on silver bromide. Solutions of silver halides in allyl thiocarbamide, like those in sodium thiosuplhate, are stable only in the presence of a large excess of the solvent. Under the conditions of sensitization, the solution is continually saturated with silver bromide and hence at its minimum stability. It seems possible that even in the emulsion the reaction may go on by decomposition of the solution.

The data on kinetics are not sufficient to formulate any mechanism consistent with the chemistry of the system. It may be noted that two hydrogen ions must be liberated by the decomposition of the silver bromide-thiocarbamide complex to form one Ag_2S, so that the reaction would be expected to be highly sensitive to hydrogen-ion concentration. The bromide ions, liberated when the complex ion was formed, affect the velocity through their effect on the solubility equilibrium.

The effect of the gelatin on the catalysis of the reaction by silver sulphide cannot be satisfactorily explained. If there were only the case of the "grainless" emulsions, it would appear that the gelatin simply retarded the crystallization of silver sulphide. The effect of the gelatin, however, nearly vanished in the normal emulsions, although the total gelatin concentration was the same.

The kinetic data on the sulphite reaction leave its mechanism in doubt. The low apparent order is rather remarkable, since by any conceivable mechanism hydrogen ions must be formed in the final step, and the equilibrium in solution must be dependent on bromide-ion concentration. The effect of gelatin on reaction velocity is consistent with its known tendency to retard the crystallization of silver

from solution. The reaction was catalyzed by metallic silver. This has already been observed (10) (11) in the precipitation of silver from solutions of silver sulphite in sodium sulphite. The probability that the reaction takes place at the solid silver bromide in preference to the dissolved silver salts seems small; there was no evidence that the rate of reaction was dependent on the amount of solid silver bromide. Since photographic sensitization was obtained under conditions only slightly removed from those of our kinetic experiments, it appears very probable that sensitization was produced by precipitation of silver on the silver bromide from the solution phase.

We have already pointed out (6) that the photographic evidence on after-ripening suggests that the formation of sensitivity nuclei is an autocatalytic process. The data in this paper show that this is actually the case. Furthermore, it seems possible that the autocatalysis is a necessary condition for sensitization. If it exists, the silver sulphide or silver will tend to build up on the first particles formed, decreasing the number and increasing the average size of the nuclei. Reinders and Hamburger have recently calculated the probabilities of a purely random distribution of silver sulphide over the surface of silver bromide grains in the quantities involved in sentitization, showing that aggregates as large as 3 or 4 molecules would be of very infrequent occurrence. They have presented evidence which they have interpreted to show that, under favorable conditions, aggregates of this size may serve as centers for physical development. However, the random distribution seems probable only for instantaneous ionic reactions such as that with sodium sulphide, which does not produce sensitization. We therefore suggest that autocatalytic reactions, such as those with allyl thiocarbamide or sodium sulphite, favor sensitization because they avoid the relatively uniform distribution of silver sulphide or silver which is characteristic of instantaneous ionic reactions. Sheppard's observation that the sensitizers must form molecular complexes with the silver halides has been supported by the discovery of the sensitizing property of sodium sulphite. Our interpretation of the necessity for this condition is different from that of Sheppard. We believe that it is characteristic of sensitizers because it is characteristic of slow, autocatalytic reactions as contrasted to instantaneous ionic reactions.

We are indebted to Dr. P. H. Emmett, of the Bureau of Chemistry and Soils, for advice and suggestions used in interpreting the data and in planning some of the experiments.

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SOURCES OF ERROR IN MEASURING OPACITY OF PAPER BY THE CONTRAST-RATIO METHOD

By Deane B. Judd

ABSTRACT

Contrast ratio of a paper sample is defined as the brightness of the illuminated sample when backed by a black-lined cavity divided by its brightness when backed by a surface of magnesium oxide. In practice other less fragile surfaces are substituted for the MgO surface, and to protect these substitute surfaces as well as the paper samples themselves the samples are kept from touching the surfaces. Both departures from the definition are potential sources of error. These errors have been investigated experimentally and a theoretical expression representing them is given.

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I. INTRODUCTION

Contrast ratio of any thin sample is defined[1] as the brightness of the illuminated sample when backed by a black-lined cavity divided by its brightness when identically illuminated and backed by a surface of magnesium oxide. This ratio has been found of use in specifying tracing cloth, glassine paper, and envelope windows,[2] in which case a low value is desired, and in specifying printing paper[3] in which case a high value is desired. The present discussion deals particularly with the latter case, the experimental data referring to samples of contrast ratio greater than 0.50; furthermore, the derivations depend on the assumption that the light reflected and transmitted by the sample is completely diffused. Hence, the conclusions may not be

[1] Circular of the Bureau of Standards 63, Specification of the Transparency of Paper and Tracing Cloth, May 17, 1917.

[2] I. G. Priest, The Bureau of Standards Contrast Method for Measuring Transparency, Trans. Amer. Ceramic Soc., vol. 17, p. 150, 1915. R. E. Lofton, Study of the Windows of Window Envelopes for the Purpose of Developing Standard Specifications, B.S. Technologic Paper 343, vol. 21, pp. 385–399, 1926–27.

[3] Used by the Government Printing Office in the purchase of printing papers. See also C. F. Sammet, A Measurement of the Translucency of Papers, U.S. Bureau of Chemistry Circular no. 96, 1912. J. d'A. Clark, The Measurement of the Contrast Ratio of Opaque and Translucent Papers, Paper Trade Journal, vol. 89, November 14, 1929. M. N. Davis, Methods and Instruments for Opacity Measurement, Tech. Assoc. Papers, series 15, pp. 347–350, 1932. M. N. Davis, A Simple and Reliable Photo-Electric Opacity Tester, Tech. Assoc. Papers, series 16, pp. 277–279, 1933.

valid for tracing cloth, glassine paper, and the like, and should not be applied to them without further inquiry.

Although the definition of contrast ratio is in terms of a surface of magnesium oxide nearly in contact with the test specimen,[4] actual instruments for the measurement of opacity by the contrast-ratio method use a less fragile surface (usually magnesium carbonate) separated sometimes as much as 2 mm from the test specimen, and sometimes further protected from injury by interposition of a thin cover glass. It is the purpose of the present paper to investigate the errors in contrast ratio which may arise (1) from departure of the reflectance of the working standard white surface from that of the standard MgO surface, and (2) from separation of the white surface from the test specimen.

II. DERIVATION OF FORMULAS

The following symbols will be used:

$C_{R,t} \equiv$ ratio of brightness of illuminated sample backed by a cavity reflecting no light to its brightness when identically illuminated and backed by a surface of reflectance, R, at a distance, t.

$C \equiv$ an abbreviation for $C_{1,0}$ which refers to contact with a perfectly reflecting surface ($R=1$, $t=0$).

$f \equiv$ flux incident per unit area on the sample.

$f_0 \equiv$ flux reflected per unit area of the sample when backed by the cavity of zero reflectance.

$f_{R,t} \equiv$ flux reflected per unit area of the sample backed by a surface of reflectance, R, at a distance, t.

First the connection will be found between the measured contrast ratio, $C_{R,t}$, and the reflectance, R, of the white backing whose distance from a thin, nonabsorbing, perfectly diffusing, test specimen is so small that further decrease makes no difference in the measured ratio ($t=0$); that is, $C_{R,0}$ will be found as a function of R. Since the test specimen does not absorb any light, we may write:

$$f \equiv f_{1,0} = f_0 + (f_{1,0} - f_0) \tag{1}$$

$$C \equiv f_0/f_{1,0} = f_0/f \tag{2}$$

It is seen from equation (1) that the incident flux may be thought of as divided into two parts, first, that reflected from the cavity-backed sample, f_0, and, second, that transmitted into the cavity, $f_{1,0}-f_0$. If now the surface of reflectance, R, be substituted for the black-lined cavity, the flux, $f_{1,0}-f_0$, illuminates the surface which returns an amount, $(f_{1,0}-f_0)R$, to the back side of the test specimen. Part of this flux passes through the test specimen which from equation (2) may be written $(f_{1,0}-f_0)R(1-C)$, while the rest, $(f_{1,0}-f_0)RC$ is reflected back to the surface of reflectance, R, and so on. The total flux passing through the sample due to these multiple reflections may be represented by an infinite series which, when added to

[4] Official Method of the Technical Association of the Pulp and Paper Industry for Determination of Opacity of Paper (no. T425m, obtainable from the association at 370 Lexington Ave., New York, N.Y.), states in this connection, "The white standard surface must not touch the surface of the test specimen but must be so near it that a further decrease in distance will not affect the test results."

the flux, f_0, reflected from the sample, makes up the whole flux leaving the surface, $f_{R,0}$:

$$\begin{aligned} f_{R,0} &= f_0 + (f_{1,0} - f_0)R(1-C) + (f_{1,0} - f_0)RCR(1-C) + \ldots \\ &= f_0 + (f_{1,0} - f_0)R(1-C)[1 + RC + (RC)^2 + (RC)^3 + \ldots] \\ &= f_0 + (f_{1,0} - f_0)R(1-C)/(1-RC) \end{aligned} \tag{3}$$

It will be noted that when $R=1$, equation (3) becomes identical with equation (1).

From the definitions of terms and equation (3):

$$\begin{aligned} C_{R,0} = f_0/f_{R,0} &= \frac{f_0}{f_0 + (f_{1,0} - f_0)R(1-C)/(1-RC)} \\ &= \frac{C}{1-(1-C)[1-R(1-C)/(1-RC)]} \end{aligned} \tag{4}$$

The derivation of $C_{R,t}$ as a function of R and t follows very similar lines. For simplicity the sample and white backing are considered to be circular of radius, r; and it is assumed that the white backing is drawn back in a tube of radius, r, whose inner walls have a reflectance, R_t. It is also assumed that the light flux is uniformly distributed over the walls of the cylindrical cavity formed between sample and white backing for t greater than zero. It is found that with these additional assumptions:

$$C_{R,t} = \frac{C}{1-(1-C)\left[1 - \frac{R_c(1-C)}{(1-R_cC)}\frac{r}{r+t}\right]} \tag{5}$$

where $R_c = (rR + 2tR_t)/(r+2t)$. Note that R_c in equation (5) replaces R in (4), it is the average reflectance of the walls of the cylindrical cavity exclusive of the front which is made up of the test specimen; when $t=0$, $R_c=R$, and equation (5) becomes identical with (4). The factor, $r/(r+t)$, appearing in the denominator takes account of the fact that the light flux in the cylindrical cavity is spread by multiple reflection over an increasing area as t increases, each reflection permitting a loss of flux by absorption not taken into account by R_c. The factor takes this simple form because of the assumption that the light flux is uniformly distributed over the walls. For very large values of t, the inaccuracy of this simplifying assumption clearly reveals itself because equation (5) then becomes: $C_{R,\infty}=1$; that is, the formula indicates that a white-lined cavity of infinite length would be equivalent to the black-lined cavity of finite length. This would be the case even for $R=1$ if the light flux could be forced to spread over the walls uniformly in accord with the assumption; actually, however, the sample would receive some light from the nearby illuminated inner wall of the tube which would make $C_{R,\infty}$ somewhat less than unity. This inaccuracy for t large is of no practical concern because in practice t is always considerably smaller than r.

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III. EXPERIMENTAL RESULTS

Equation (4) depends only on the assumption that the test specimen be a thin, nonabsorbing, perfectly diffusing sample. Since most paper samples customarily measured for opacity by the contrast-ratio

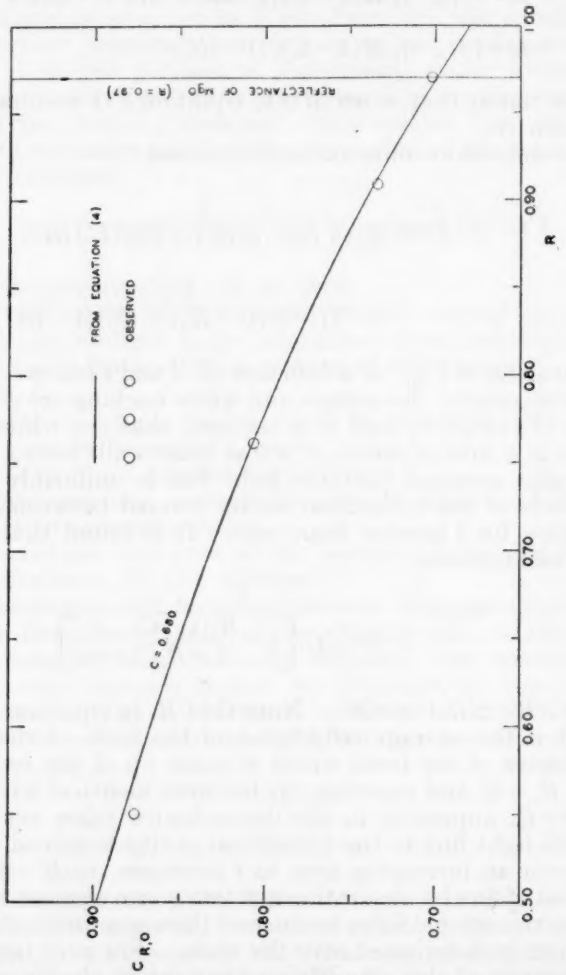

FIGURE 1.—*Measured values of contrast ratio, $C_{R,0}$, for a sample of depolished opal glass closely backed by surfaces of various reflectance, R, plotted against R.*

It is seen that equation (4) agreed well with the observed values. Note that the true value of contrast ratio, $C_{0.970,0}$, for this sample is about 0.70, while $C_{1,0}$ is about 0.68.

method satisfy these conditions fairly well, it will probably be sufficient to show that this equation adequately represents the actual relation for one fairly typical sample. The curve in figure 1 shows $C_{R,0}$ as a function of R according to equation (4) for $C=0.680$; the plotted points refer to a thin piece of opal glass depolished on both sides. The four surfaces used to back this sample were (1) light gray paper,

(2) white paper, (3) a freshly scraped magnesium carbonate block of unknown history and purity,[5] and (4) a freshly prepared surface of magnesium oxide. The reflectance of the MgO surface was taken as 0.97; [6] the reflectances of the other surfaces were measured relative to the MgO surface for diffused illumination and normal viewing. The distances between backing and sample were not zero but it is estimated that they were all less than 0.2 mm. Uncertainty as to this distance and the experimental uncertainty of setting is sufficient to account for the deviation between the plotted points and the curve representing equation (4). Note that the true contrast ratio defined in terms of MgO would be written according to the present notation $C_{0.970,0}$ not $C_{1,0}$; from the data of figure 1 it may be seen that $C_{0.970,0}$ for this sample is about 0.70, while $C_{1,0}$ is about 0.68.

Equation (5) involves the additional assumption that light flux within the cylindrical cavity is uniformly distributed. This is not strictly true for any nonspherical cavity even when the inner walls are perfectly diffusing, and for very flat cylinders such as are here considered as t approaches zero, the error may be considerable. It remains to be seen whether the relation derived from this simplifying assumption can represent experimental data on actual samples to any useful degree.

Figure 2 shows a comparison between equation (5) and experimental results on 4 samples obtained with the original model designed and used by Priest.[2] The magnesium carbonate block mentioned in connection with figure 1 was used as the white backing; the samples of highest and lowest opacity were paper, the samples of intermediate opacity were depolished opal glass. The constants used in equation (5) to represent the performance of this particular instrument are: $r=20$ mm, $R=0.91$, $R_t=0.50$. The radius of the circular sample and the reflectance of the $MgCO_3$ surface are, of course, accurately known, but the reflectance, R_t, of the inner walls of the imaginary cylinder was rather arbitrarily set at 0.5 because such a value gave a satisfactory fit for the data. The actual reflectance, R_t, is not a constant but decreases somewhat with increasing t.

It will be noted that equation (5) may be made to describe the performance of this particular instrument with fair accuracy. There is a tendency, which is probably significant, for the observed points to be high for t nearly zero; such an increase suggests that the assumption of equal distribution of light within the cylindrical cavity is producing appreciable error. There is also a significant tendency for the observed points to be high for large values of t; this may be ascribed to the decrease in the actual value of R_t as t increases which is not taken account of by equation (5).

[5] Although $MgCO_3$ blocks are widely used because of their convenience and cheapness to provide surfaces of constant reflectance nearly equal to unity, there is considerable doubt whether much reliance should be placed on such surfaces. It is known (Priest, Jour. Opt. Soc. Am. and Rev. Sci. Inst., vol. 20, p. 157, 1930; Pfund, Jour. Franklin Inst., vol. 189, p. 378, 1920; Hyde, Astrophys, Jour., vol. 35, p. 239, 1912) that commercial $MgCO_3$ is yellow. Furthermore, some of the commercial product has been found to be much yellower and darker than the usual product, exposure to strong light has been known to darken and yellow a block of $MgCO_3$ to a considerable depth beneath the exposed surface, and nothing is known of the permanence of the reflectance of pure samples kept shielded from light. The block of $MgCO_3$ used here is an example of the possible variation. It was found by comparison with MgO to have a reflectance of 0.91 (see fig. 1); this value is importantly lower than the accepted value, 0.98, given in the International Critical Tables.

[6] International Critical Tables, vol. 5, p. 262. Also Preston, The Reflection Factor of Magnesium Oxide, Trans. Opt. Soc., vol. 31, p. 29, 1929–30.

A similar, though less extensive, investigation of another design of opacimeter has revealed considerably larger variation in measured values of contrast ratio as t is varied. Equation (5), however, yields

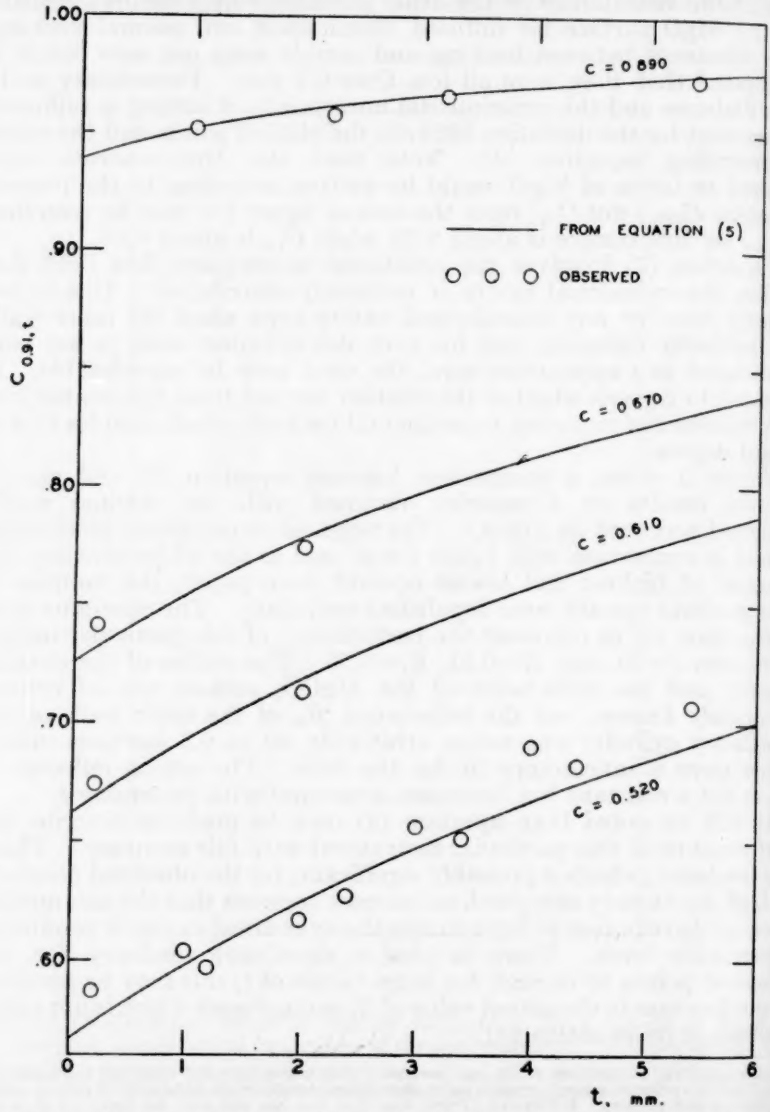

FIGURE 2.—*Measured values of contrast ratio, $C_{0.91,t}$, for four samples as a function of the distance, t, between sample and the working standard* $MgCO_3$ *surface whose reflectance, R, is 0.91.*

It is seen that equation (5) is in fair agreement with the observed values. The values of C (contrast ratio measured with the sample in contact with a perfectly reflecting white surface) substituted in equation (5) for comparison with the observed values are indicated on the graph. Note that the use of a magnesium carbonate surface of low reflectance (0.91) separated from the sample by 2 mm may result in measured values of contrast ratio too high by as much as 0.08.

this result also because of the smaller radius of sample effective in this instrument; and it may be made to represent the performance of this opacimeter with the same degree of accuracy.

IV. CONCLUSIONS

The following conclusions seem justified from the foregoing experimental and theoretical results.

1. Measured values of contrast ratio for paper depend to an important extent on the reflectance of the standard white surface which backs the test specimen. The use of magnesium carbonate as a substitute for magnesium oxide may introduce errors as large as 0.03 or 0.04 in measured values of contrast ratio for paper (see fig. 1, measured value, more than 0.73; true value, 0.70).

2. The derivation of equation (4) connecting measured contrast ratio with reflectance of the standard white surface makes feasible the use of permanent surfaces such as porcelain or opal glass as substitutes for the fragile MgO standard surface, or the impermanent $MgCO_3$ surface often used as a working standard. A measurement of reflectance relative to MgO combined with application of equation (4) would suffice to calibrate the instrument for samples which, like paper, absorb but little light.

3. Measured values of contrast ratio for paper depend to an important extent on the degree of separation between test specimen and white backing. A separation of 2 mm for a sample as large as 40 mm in diameter (see fig. 2) may yield measured values of contrast ratio higher by 0.03 or 0.04 than the values yielded by a separation of 0.2 mm.

4. If the distance between test specimen and white backing be accurately controlled at some definite value (say 2 mm) the readings may be approximately corrected for the error so introduced by application of equation (5),[7] but a more satisfactory solution is to be obtained by using a permanent working standard white backing such as porcelain or opal glass in which case the test specimen may be placed in contact with the white backing in exact conformity to the definition of contrast ratio.

WASHINGTON, October 1933.

[7] If the separation of sample and backing be controlled by interposition of a piece of glass, the effective separation (that is, the value of t to be substituted in equation (5)) is less than the actual separation because of refraction of light at the glass surface near the sample. Any appreciable absorption of light by the glass would also have to be taken into account.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP661

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ERRORS IN GAS ANALYSIS ARISING FROM LOSS OF GAS BY SOLUTION IN RUBBER CONNECTIONS AND STOPCOCK LUBRICANT

By Joseph R. Branham

ABSTRACT

This paper presents experimental data on the loss, by solution, of certain gases in the rubber connections and stopcock lubricant of volumetric gas-analysis apparatus. It is shown that errors, which may be serious, result whenever high concentrations of carbon dioxide, ethane, ethylene, acetylene, propane, propylene, or butane are present in such apparatus. A method of obtaining an approximate correction by means of a blank analysis is proposed. This correction improves the accuracy of the analysis, but with gases which are very soluble, such as propylene and butane, the results, while improved, are still very unsatisfactory.

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INTRODUCTION

Modern volumetric gas-analysis apparatus is generally of the type which employs a distributor (or manifold) to connect the burette with the various pipettes. For necessary convenience, the separate parts of such apparatus are connected by means of rubber tubing. These connections are made by placing a rubber sleeve over glass capillary tubes, the ends of which are closely butted together. When such a joint is properly made and secured,[1] it may be depended upon to cause no ordinary leakage under the conditions existing during an analysis.[2]

[1] In assembling such connections, the glass capillaries should be ground flat at the ends, so that a minimum surface of rubber is exposed. The rubber sleeve should be secured at both ends by tightly wrapped waxed dental floss.

[2] For example, many repeated routine tests have shown that no measurable leakage occurs when air is contained in the apparatus at pressures both greater and less than atmospheric. Such tests extend over a period exceeding that required for an analysis, and the pressure differences imposed are greater than will occur during an analysis.

It is well known, however, that many gases are soluble in rubber. Some of these gases may be encountered in samples to be analyzed, and one at least—carbon dioxide—occurs regularly during the majority of combustion analyses. In addition, it is known that many gases, particularly the hydrocarbons, are soluble in the greases which are used to lubricate the stopcocks of gas-analysis apparatus.

It has previously been supposed (insofar as ordinary gas analysis is concerned) that no significant amounts of gases would be lost by solution in the small surface of rubber exposed by connections such as those described, or by solution in the lubricant of stopcocks. The purpose of this paper is to report experimental data showing that significant amounts of various gases are lost by such solution, and that the errors caused by such losses are frequently significant and sometimes large.

In order to picture the possibilities involved, a brief outline will be given for the procedure of an ordinary combustion analysis.

1. A volume of oxygen in excess of that required for the proposed reaction is measured in the burette and transferred to the combustion pipette.

2. The sample to be burned is measured in the burette, whence it is passed very slowly into the combustion pipette, and reacts with oxygen in the presence of hot platinum. Thereafter the mixture present is repeatedly passed back and forth between burette and pipette until the reaction is completed. (The volume of the sample is hereafter identified as *S*.)

3. The products of combustion are allowed to cool in the combustion pipette, and are then returned to the burette where the contraction resulting from the reaction is measured. (This volume is hereafter identified by the symbol *TC*.)

4. The volume of carbon dioxide produced by the reaction is then determined. (This is identified as CO_2.)

5. The excess oxygen is then determined, and from this volume of oxygen consumed (O_2) is obtained.

Since the three factors—*TC*, CO_2, and O_2—are used to calculate the nature and amounts of the combustible gases, it is obvious that any loss of gas during any process involved in obtaining these values will cause an error in the computation. Furthermore, the effect of small losses will usually be magnified by the mathematics of the computation.[3]

Step number 2 of the procedure outlined is the one during which such losses are very troublesome. This may happen as follows:

(*a*) If the sample contains a gas which is soluble in lubricant or rubber, significant amounts of this may be lost during its measurement. In some cases, it was found that no reliable measurement could be made, since solution occurred at a rate rapid enough to prevent adjustment of the pressure of the sample to the fixed reference pressure.

(*b*) If the sample contains a gas which is soluble in lubricant or rubber, a significant amount may be lost during the slow passage into the combustion pipette. Some of the gas so lost will never reach the reaction zone. A part of it may reappear when the products of combustion are returned to the burette, with the possibility of burn-

[3] The reader who is not familiar with the general procedure and computation of gas analysis may supplement the general picture given here by referring to any good text on the subject, or to B.S. Research Paper 266.

ing during the later passages into the combustion pipette. Such losses will affect *TC*, CO_2, and O_2.

The problem is somewhat complicated when consideration is given to the actual behavior of the dissolved gases. In general, two things may be expected to occur: 1. When a gas dissolves in the rubber tubing, a portion of it may completely penetrate the tubing and be given up to the air outside of the apparatus. This will produce the same effect, as far as the analysis is concerned, as though actual leakage had occurred during the particular procedure involved. 2. Some of the dissolved gas will remain in the rubber (and lubricant) until a gas of a different composition is brought into contact with the rubber and lubricant within the apparatus. The dissolved gas will then begin to reappear as a contamination, thus changing the volumes and introducing errors.

It is consequently possible to lose some gas altogether, and to lose a gas during one step of the analysis only to regain a portion of it during subsequent steps or subsequent analyses.

(*c*) The carbon dioxide produced during the combustion is in contact with rubber and lubricant at all times after the initial passage of the sample into the combustion pipette, and until it is finally removed in step number 4. Any carbon dioxide lost during this period will affect both *TC* and CO_2.

In order to establish the probable errors caused by such losses, measurements were made of the rate of solution of various gases. These measurements were conducted:

1. In the gas analysis apparatus, as used in general practice.
2. With the distributing train replaced by 8-cm lengths of different rubber tubes. (To magnify the losses caused by rubber connections.)
3. With the distributing train replaced by an 8-cm length of glass tubing coated inside with different lubricants. (To magnify losses caused by lubricated stopcocks.)

II. APPARATUS

The apparatus used in the experiments was that described by Shepherd.[4] The gas comes in contact with two rubber connections when passed between the burette and any pipette. In addition, one rubber connection between the compensating unit and the distributing train is involved to a greater or lesser degree, during the measurement of any gas. Unless otherwise specified the rubber was pure gum, acid cured, with 5-mm bore and 1.75-mm wall.

The stopcock grease employed was made of rubber, vaseline, and paraffin in the manner described by Shepherd and Ledig.[5] The gases used were carbon dioxide, acetylene, ethylene, ethane, propane, propylene, and butane; all were thought to be reasonably pure, but only in the case of the ethane and carbon dioxide was the purity known.

III. EXPERIMENTAL PROCEDURE

Two methods of measurement were employed. The first was to set up a condition in the apparatus approximating that of the usual analytical procedure. The distributing train and manometer were filled with nitrogen at the pressure (nearly atmospheric) at which the

[4] An Improved Apparatus and Method for the Analysis of Gas Mixtures by Combustion and Absorption. Martin Shepherd, B.S. Jour. Research, vol. 6 (RP266), p. 121, 1931.
[5] Ind. Eng. Chem., vol. 10, p. 1059, 1927.

manometer balanced. The sampling leads to the burette were flushed with the gas to be used, and a sample of this gas was taken into the burette under positive pressure. The stopcock at the top of the burette was then closed and the pressure of the gas adjusted to approximately atmospheric. The manometer and burette stopcocks were then opened to connect the manometer and burette. The pressure of the gas in the burette was then adjusted to the fixed pressure of the compensator, and its volume read. This procedure was employed to prevent, as far as possible, the mixing of the sample with the nitrogen in the manometer, thereby minimizing the solution of the sample in the rubber connection between the compensator and distributing train. It is doubtful whether this was entirely successful, but some such method was necessary to obtain the original volume of the sample, particularly in the case of the more soluble gases. The samples taken were always about 20 ml. The stopcocks were then turned so that the gas in the manometer was shut off from the burette and distributor, and the burette was connected by way of the distributor and two rubber connections to the combustion pipette. This moment was taken as zero time and the gas in the burette was immediately started on a slow passage to the combustion pipette. The platinum spiral in the combustion pipette was not heated.

At convenient times over a period of 30 or more minutes the gas in the combustion pipette was returned to the burette and its volume determined. The difference between the original volume at zero time and the volume at any subsequent time is the loss attributed to the solution of the gas in the rubber connections and stopcock lubricant. The data obtained were recorded as elapsed time compared with the corresponding loss of volume.

The procedure described is essentially a blank analysis. A procedure of this general type may be devised for any particular case, so that it will afford corrections to be applied to a corresponding analysis. However, the losses measured were sometimes small, and did not always exceed the limiting accuracy of the volumetric system sufficiently to justify rigid conclusions. Therefore, a second method was employed which purposely magnified the losses previously observed.

The second method employed was to replace the distributing train and combustion pipette by a piece of rubber tube about 8-cm long, or with a piece of glass tubing of the same length coated on the inside with vaseline or other stopcock lubricant. The exit end of the rubber or glass tube terminated in a stopcock so that either could be flushed out at the start of a test with a portion of the sample.

The procedure was to take a sample of about 80 ml into the burette and to flush about 60 ml of it through the stopcock at the end of the tube which replaced the distributing train. After closing this stopcock the volume remaining was determined, observing the same precautions described for the first method. The time at which this initial volume was determined was taken as zero time. At convenient intervals the manometer was rebalanced and the volume at manometer pressure determined. In this manner, data were obtained confirming the smaller (and more difficultly measurable) losses obtained with the combustion pipette and distributing train. The second method is open to the serious objection that at zero time the rubber tube (or lubricant) is partially saturated with gas and consequently the measured losses are lower than otherwise would have been obtained.

IV. EXPERIMENTAL RESULTS

1. RESULTS OF BLANK ANALYSES WITH REGULAR APPARATUS (METHOD 1)

The experimental data obtained by both methods are presented in the form of curves, the ordinates of which are elapsed time in minutes and the abscissas are milliliters of gas lost by solution.

The losses by solution which result when various gases are subjected to the analytical manipulations corresponding to a combustion and the measurement of the resulting contraction are shown in figure 1.

The data do not justify drawing separate curves for the four less soluble gases, i.e., carbon dioxide, acetylene, ethylene, and ethane,

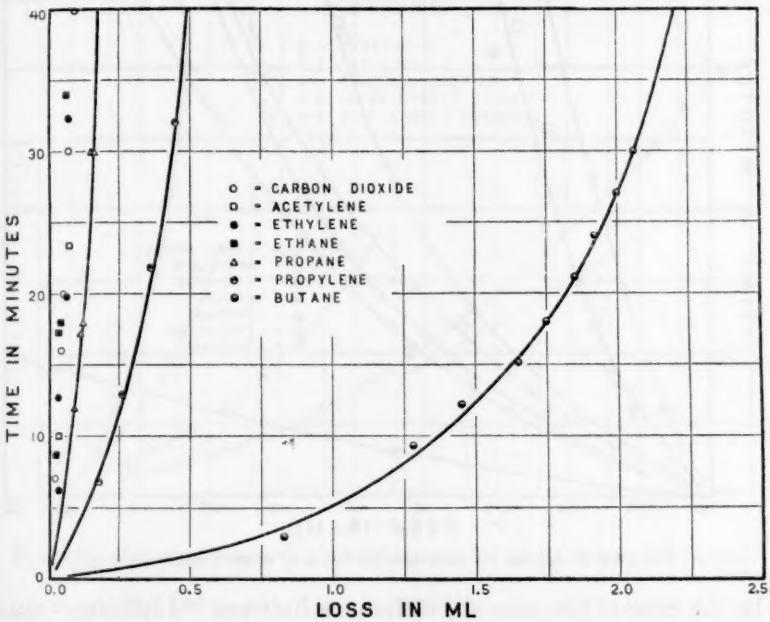

FIGURE 1.—*Loss by solution in the distributor of the gas analysis apparatus.*

and no conclusion may be drawn other than that their rates of solution are of the same order of magnitude. The curves for propane, propylene, and butane are satisfactorily smooth and indicate increasing rates of solution for these gases in the order given. The smoothness of the curves does not, however, justify their use as a direct correction to be applied to analytical results because, as will be shown in figure 2, they represent what may be expected only under the particular set of conditions prevailing when the tests were made.

2. RESULTS OBTAINED BY METHOD 2 (MAGNIFIED RATES OF SOLUTION)

(a) LOSS OF VARIOUS GASES IN RUBBER TUBING

The curves of figure 2 represent the data obtained when the combustion pipette and distributing train were replaced by a piece of clear rubber tubing 8-cm long.

Under these conditions the less soluble gases seem to be separated into two groups, carbon dioxide and ethylene being dissolved less rapidly than acetylene and ethane.

The curves showing the results of attempted duplicate tests for propane and propylene illustrate the change in rate of solution which may be expected with changing experimental conditions (particularly temperature), plus the manipulative error in choosing zero time. In these tests, fresh rubber tubing (of the same length and composition) was used for each determination, and the stopcocks were regreased with fresh lubricant of the same composition previously used.

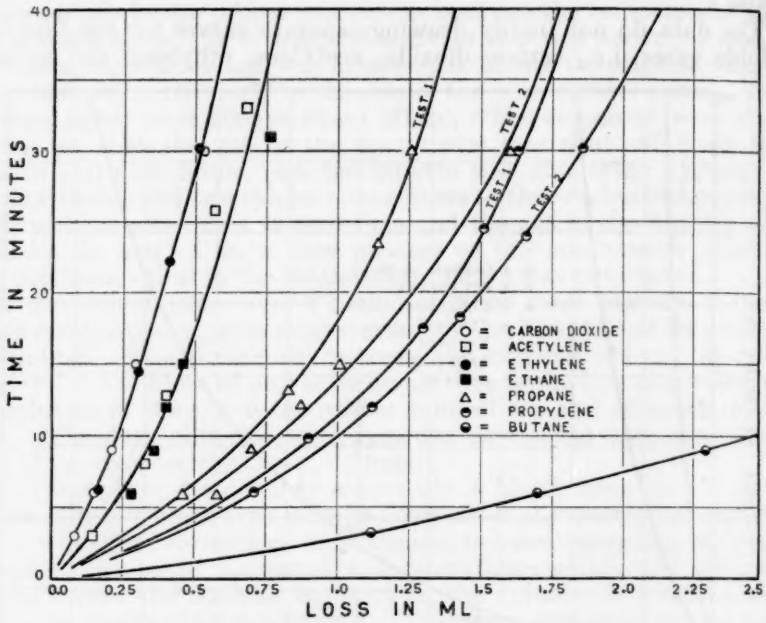

FIGURE 2.—*Loss by solution in 8 cm of clear rubber tubing.*

In the case of propane the difference between "duplicate" tests is roughtly 20 percent, and there is no reason to believe that differences greater than this may not be expected.

In view of this fact the apparent difference in behavior of carbon dioxide and ethylene shown by one curve of figure 2 from that of ethane and acetylene shown by another curve may well be accidental. In addition, it is somewhat doubtful whether results obtained by the use of relatively long rubber tubing can be applied to the loss of gas under conditions prevailing in method 1. The best conclusion that can be drawn from the data obtained is that the losses of carbon dioxide, ethane, acetylene, and ethylene are all of the same order of magnitude.

(b) LOSSES OF BUTANE WITH GRAY RUBBER TUBING AND WITH LUBRICANTS OF DIFFERENT COMPOSITIONS

In order to establish the magnitude of losses of gas by solution in different lubricants and in gray rubber tubing the data given in figure 3 were obtained. The data obtained with butane in the

unmodified apparatus, figure 1, and with butane in the clear rubber tubing, figure 2, are included for comparison.

The inside dimensions of the glass tube used to obtain the data shown by the curves in figure 3 were approximately the same as those of the rubber tube used for figure 2. The glass was coated on the inside with a thick layer of vaseline or stopcock lubricant, but these layers were not necessarily of the same thickness in the two cases. Very little discussion of these results seems necessary, and it will suffice to say that while gray rubber tubing seems to cause a greater loss than clear rubber tubing, and a greater solubility was indicated in

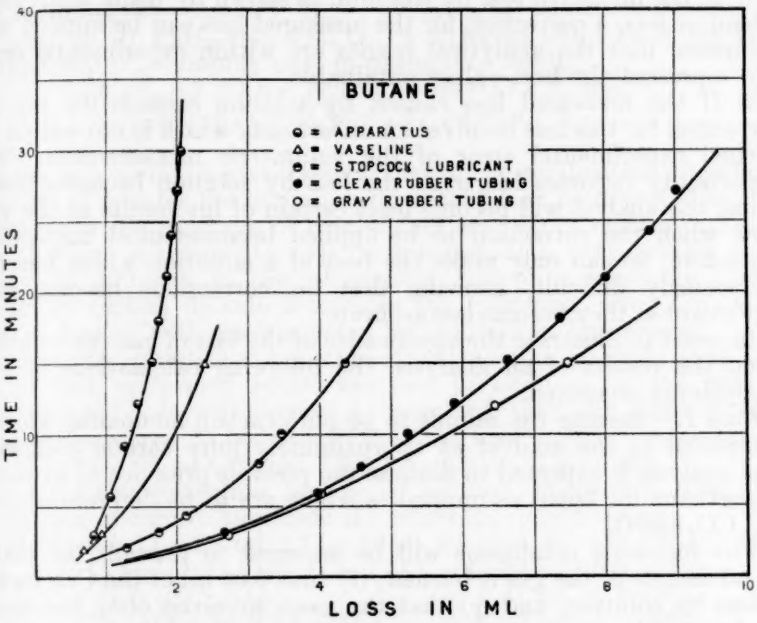

FIGURE 3.—*Loss of butane by solution in rubber tubing and in lubricants.*

the compounded lubricant than in vaseline, the differences have no practical significance as far as an analysis is concerned.

V. APPLICATION TO ANALYTICAL RESULTS

The data indicate that a correction for gas lost by solution in rubber connections and stopcock lubricant is desirable if errors caused by solution are to be avoided in gas analysis.

Since the corrections to be made will vary with each apparatus and the conditions under which it is operated, satisfactory corrections can be deduced only by performing blank analyses in connection with the analyses to which the corrections are to be applied. The blank analysis should be designed so that they will indicate the volume of gas lost by solution and also the volume of dissolved gas that may come out of solution from the connections and lubricant when a different gas is present in the apparatus. This second requirement is particularly important when dealing with the more soluble gases.

It is obvious that the value of blank analyses depend upon how closely they predict what will occur in the analyses to which they are applied. Furthermore, it can be seen that the effect of a variation of time or other condition between the blank and the actual analysis will be more serious when dealing with gases whose rates of solution are rapid.

If the probable error in the measurement of any gas volume is ± 0.02 ml and the probable error in the measurement of the loss of gas by solution (in rubber and lubricant) is ± 20 percent, the following facts obtain:

1. If the measured loss by solution, as shown by blank analyses, is 0.1 ml or less, a correction for the measured loss can be applied with assurance that the analytical results are within experimental error, and represent the best values obtainable.

2. If the measured loss caused by solution exceeds 0.1 ml, the correction for this loss involves an uncertainty which is not within the normal experimental error of the volumetric measurement. This uncertainty becomes larger as the loss by solution becomes larger. Thus, the analyst will become least certain of his results at the very time when the correction to be applied becomes most imperative. Therefore, he can only make the best of a situation which becomes increasingly difficult, knowing that his corrections become more significant as they become less accurate.

In order to illustrate the significance of the loss of gas (by solution) upon the results of an analysis, the following calculations of such analysis are presented:

Case 1.—Assume the sample to be pure carbon monoxide, which is submitted to the analyst as approximately pure carbon monoxide. The analysis is expected to disclose the possible presence of hydrogen or methane (or both) as impurities which are to be determined from *TC*, CO_2 and O_2.

The following conditions will be assumed to prevail: (*a*) that a 50 ml sample of the gas is burned; (*b*) that 0.06 ml of the CO_2 formed is lost by solution, and (*c*) that the gases involved obey the simple gas laws.

Under these conditions the data obtained would be $O_2 = 25.00$ ml, $CO_2 = 49.94$ ml and $TC = 25.06$ ml, and the following results would be reported:

$$\begin{aligned} CO &= \tfrac{1}{3}(4\ CO_2 + TC - 3\ O_2) = 49.94 \text{ ml} = 99.88\% \\ H_2 &= (TC - O_2) = .06 \text{ ml} = .12\% \\ CH_4 &= O_2 - \tfrac{1}{3}(CO_2 + TC) = .00 \text{ ml} = .00\% \end{aligned}$$

Case 2.—Assume the sample to be pure butane, which is submitted to the analyst to determine the possible presence of propane. Since it is normal practice to calculate the percentages of these two gases from *TC* and CO_2, these factors will be used in the illustrative example. (Such a procedure is not recommended, but is followed here simply because it represents the usual routine.)

The following conditions will be assumed to prevail during analysis: (*a*) that a 10 ml sample of the gas was analyzed. (The size of the sample is limited by the amount of oxygen necessary to burn it. The oxygen must be present in large excess, and must be measured in the burette); (*b*) that 1.0 ml of the sample was lost by solution. (The data given show a loss of 1.8 ml, but other observations show that approximately 0.8 ml of the gas so lost will be regained in 20 minutes

in the presence of a different gas); (*c*) that 0.06 ml of the CO_2 formed is lost by solution; and (*d*) that the gases involved obey the simple gas laws.

Under these conditions, the data obtained would be:

$$S=10 \quad O_2=58.5, \quad CO_2=35.94, \quad \text{and} \quad TC=32.56.$$

This is deduced as follows:

Assuming (*a*) and (*d*)

$$10 \text{ ml } C_4H_{10}+65\text{ml } O_2 \rightarrow 40 \text{ ml } CO_2+35 \text{ ml } TC.$$

Then assuming (*b*)

$$9 \text{ ml (read as 10) } C_4H_{10}+58.5 \text{ ml } O_2 \rightarrow 36 \text{ ml } CO_2+32.5 \text{ ml } TC.$$

And assuming (*c*)

$$9\text{ml (read as 10) } C_4H_{10}+58.5 \text{ ml } O_2 \rightarrow 35.94 \text{ ml } CO_2+32.56 \text{ ml } TC.$$

By the formula commonly used in computing results,

$$C_4H_{10}=2\ (CO_2-TC)=6.76 \text{ ml}=67.6\%, \text{ and}$$

$$C_3H_8=\frac{8TC-7CO_2}{3}=2.97 \text{ ml}=29.7\%$$

In the two examples given above, that of the combustion of carbon monoxide illustrates the minimum error that may be expected in the results when the products of combustion are rich in carbon dioxide. Case 2 which involves the loss by solution of a very soluble gas, butane, in addition to the subsequent loss of a relatively small amount of carbon dioxide illustrates the maximum error that will occur in dealing with gases covered by the data in this paper.

In order to complete the picture it will now be assumed that the analyst had performed blank analyses in addition to the actual analyses cited. It will further be assumed that the error in the blank analysis was 20 percent so that the loss by solution assumed was $.80\times.06=.05$ ml CO_2 and $.80\times1.0=0.8$ ml of butane.

Applying this correction, for loss by solution, to the data from the combustion of carbon monoxide the corrected data become:

$$S=50 \text{ ml}, \quad O_2=25 \text{ ml}, \quad CO_2=49.99 \text{ ml}, \text{ and } TC=25.01 \text{ ml}.$$

$$CO=\tfrac{1}{3}\ (4\ CO_2+TC-3\ O_2) = 49.99 \text{ ml} = 99.98\%$$

$$H_2=(TC-O_2) = 0.01 \text{ ml} = 0.02\%$$

$$CH_4=O_2-\tfrac{1}{3}\ (CO_2+TC) = 0.00 \text{ ml} = .00\%$$

Applying the two "corrections" for loss by solution to the data obtained from the combustion of butane, the "corrected" data become:

$$S \text{ (burned)}=10.0 \text{ ml}-0.8 \text{ ml} = 9.2 \text{ ml}.$$

$$CO_2=39.94 \text{ ml}+0.05 \text{ ml} = 35.99 \text{ ml}.$$

$$TC=32.56 \text{ ml}-0.05 \text{ ml}-0.8 \text{ ml} = 31.71 \text{ ml}$$

$$O_2=58.5 \text{ ml}.$$

Substituting these values in the formulas,

$$C_4H_{10} = 2\ (CO_2-TC) = 8.56 \text{ ml} = 93.04\%.$$

$$C_3H_8 = \frac{8TC-7CO_2}{3} = 0.58 \text{ ml} = 6.30\%.$$

CONCLUSION

It is customary for the gas analyst to perform two or more analyses with each gas sample in order to confirm the validity of the reported data. The analytical manipulations of these "check" analyses are naturally nearly identical. If the data obtained from the second analysis agrees with the first, the conclusion is that the data are as good as may be obtained under the conditions of the analyses and

the limitations of the apparatus. These limitations or inherent errors, such as loss of gas by solution, are particularly insiduous because they may occur to the same extent in several check analyses and therefore remain hidden. Under such conditions the analyst may be misled regarding the accuracy of the analytical data, and draw erroneous conclusions concerning the composition of the samples.

Losses of hydrocarbons and carbon dioxide and, in some cases, contamination of a fresh sample with residues of gases previously analyzed, may be expected to result from the solubility of hydrocarbons and carbon dioxide in rubber tubing and stopcock grease. In some cases the error introduced may be very large, in other cases it is near the limit of observation. The analyst should have the possibility of such errors in mind at all times and should take such precautions as may be necessary to obtain results within the limit of accuracy needed for the purpose for which the analysis is made. In some cases, the necessary accuracy may be secured by making determinations of and correcting for the loss of gas which takes place in the apparatus.

WASHINGTON, January 13, 1934.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP662

Part of Bureau of Standards Journal of Research, vol. 12, 1934

TEST OF A FLAT STEEL-PLATE FLOOR UNDER LOADS

By L. B. Tuckerman, A. H. Stang, and W. R. Osgood

ABSTRACT

In cooperation with the American Institute of Steel Construction, Inc., a flat steel-plate floor was tested under loads to determine its strength and whether the floor behaved as a unit when loads were applied. The span was 18 ft. and the floor was built of 4-in 7.7-lb per ft steel I-beams and steel plates, 24-in wide and ¼-in thick. Strain-gage and deflection readings were taken.

Continuous manual welds joining the plates to the I-beams, made by using bare metallic electrodes (5/32-in diameter) and the direct-current arc-welding process, united the plates and the beams so that they behaved as a unit when loads were applied.

The measured stresses and the measured deflections were in substantial agreement with values computed by the ordinary theory of beams.

This floor carried a load of 420 lb per sq ft for 5½ days without any indication of collapse. The deflection under this load was 3⅞ in. After this load was removed the permanent deflection was 2¾ in.

The results of this test give no indication as to the maximum spacing of the beams for which the entire width of the plate is effective. The results indicate that for ordinary spans if the spacing of the beams does not exceed 100 times the thickness of the plate the entire width may be assumed effective when designing a flat steel-plate floor of the type tested.

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I. INTRODUCTION

The American Institute of Steel Construction has developed a type of floor which they call a "battledeck floor." Such a floor consists

of rolled steel I-beams and steel plates laid parallel to the beams so that the joints are over the middle of the upper flange. The edges of the plates are not in contact but are separated a distance about equal to the thickness of the plates. The plates are welded to each other and to the flange of the I-beam. The welds may be either continuous or intermittent.

The floor may be fireproofed. If resistance to fire is not necessary, linoleum, rubber tile, etc., may be applied directly to the upper surface of the floor.

In cooperation with the Bureau of Standards, the American Institute of Steel Construction, Inc., outlined a program to determine the strength and, also, the resistance of battledeck floors to fire.

The loading test on one floor was made by the engineering mechanics section of the Bureau. S. H. Ingberg, chief of the fire resistance section of the heat and power division, assisted in planning the loading test. The results are given in this paper.

The Institute was represented by F. H. Frankland, Director of Engineering Service. The floor was fabricated under the direction of C. W. Welch, research associate, who assisted in making the loading test.

II. PURPOSE

The loading test of this steel-plate floor was made to determine:

1. The strength of the floor.
2. Whether the following assumptions are justified:

(*a*) The floor behaves as a unit when loads are applied, i.e., the welds joining the beams and plates neither fail nor deform permanently.

(*b*) The entire width of plate between beams may be considered as effective in computing stress and deflections.

III. THE SPECIMEN

1. THE BATTLEDECK FLOOR

The test floor and the restraining frame are shown in figure 1. The floor consisted of six ¼-in steel plates and seven 4-in 7.7-lb per ft steel I-beams spaced 24 in on centers. The four middle plates were about 23¾-in wide and the two outer plates about 32⅔-in wide, extending 8½ in over the outer beams, nos. 1 and 7. The edges of the plates and the upper flanges of the beams were joined by continuous, open, square butt welds as shown in figure 2, extending the entire length of the beams. The outer plates were fastened to the outer beams by 6-by ⅜-in intermittent fillet welds between both edges of the flanges and the under side of the plates. The spaces on one side of the beam were opposite the welds on the other side; thus the total length of these welds on each outer beam was approximately equal to the length of the beam.

The I-beams of the floor were supported on angles bolted to the restraining frame of 30-in, 240-lb per ft steel I-beams reinforced by 6- by ⅝-in diaphragms. This frame was part of the fire-resistance chamber in which, for convenience, the loading test was made. There was clearance between the edges of the outer floor plates and the sides of the frame.

As shown in figure 3, the ends of the beams rested on the 3-in leg of the steel angles, *A*, 4 by 3 by ⅜ in, fastened to the frame by high-strength steel bolts, *B*, ¾-in in diameter and spaced 12 in on centers.

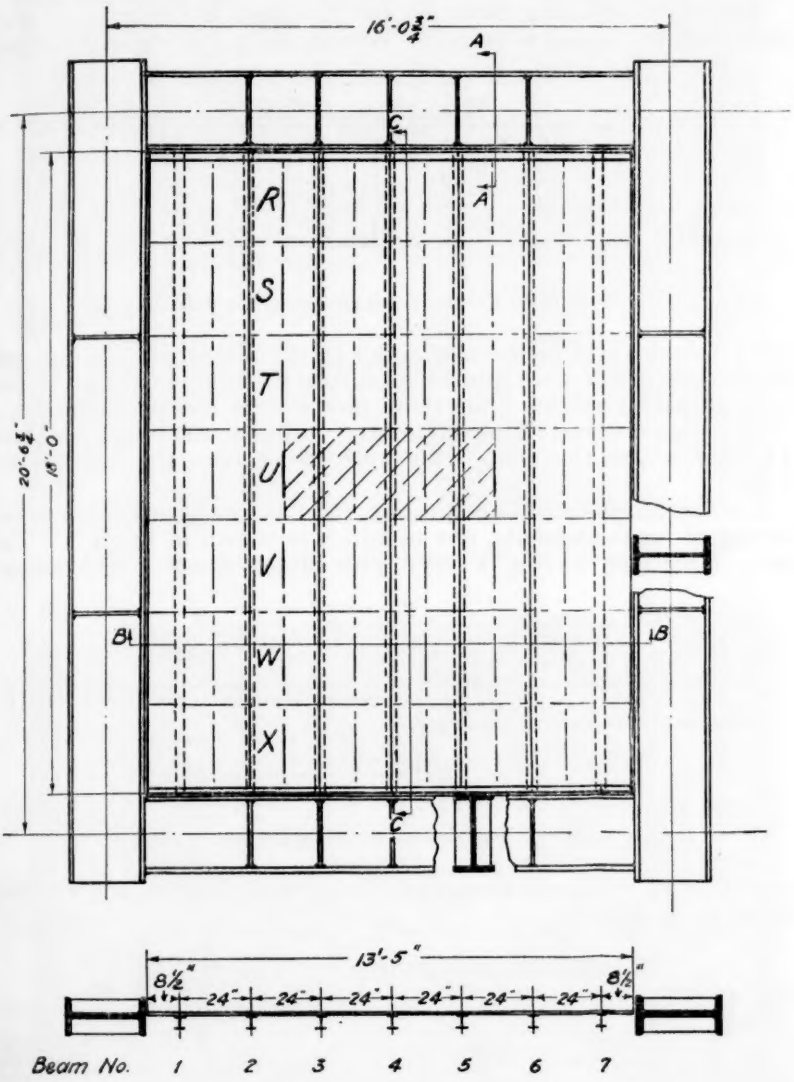

FIGURE 1.—*Battledeck floor and restraining frame.*

The bottom flanges of the beams were fastened to the angles by ⅜-in fillet welds, *C*, about 2-in long, one on each side. In order to secure an appreciable restraint at the ends of the floor, 3½- by 3- by ⅜-in steel angles, *D*, were bolted to the restraining frame by ¾-in high-strength steel bolts, *E*, spaced 12 in on centers, and the plates

were fastened to the toes of the angles by ⅜-in continuous fillet welds, *F*.

All the welds were manual, direct-current arc welds made with $\frac{5}{32}$-in bare electrodes.

The completed floor, ready for test, is shown in figure 4. It is evident that the beams were only "commercially" straight. Although

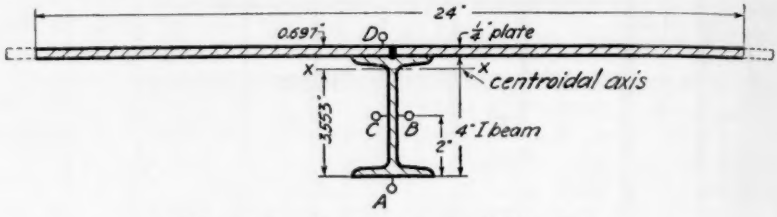

FIGURE 2.—*One beam element of the floor.*

the nominal width of the butt welds in the plates was ¼ in, in some places these welds were ⅜-in wide because the edges of the plates were not perfectly straight. Since the plates were not perfectly flat, in some places the restraining angles were not in contact with the plates. At these places the fillet welds were larger than the nominal size, ⅜ in.

For the purposes of computation the floor was considered as consisting of beam elements, one of which is shown in figure 2. They were T-sections having a very wide upper flange. The nominal

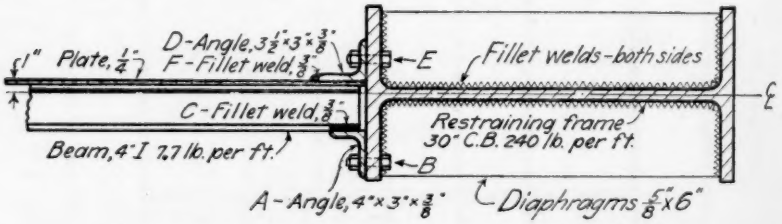

FIGURE 3.—*A longitudinal section at the end of the floor.*

properties of this beam element and therefore of the battledeck floor, are given in table 1.

TABLE 1.—*Nominal properties of the battledeck floor*

Depth of I-beam	4.0 in.
Weight of I-beam	7.7 lb per lin ft.
Thickness of plate	0.25 in.
Weight of plate and weld	20.4 lb per lin ft.
Total weight of I-beam, plate, and weld	28.1 lb per lin ft.
Average weight of floor	14.05 lb per sq ft.
Cross-sectional area (1 beam and 1 plate 24 in wide)	8.21 sq in.
Distance of the centroidal axis of the floor from the bottom of the I-beam	3.553 in.
Moment of inertia of the cross section of the floor about the centroidal axis (1 beam and 1 plate 24 in wide)	13.32 in.^{4}
Section modulus of floor (1 beam and 1 plate 24 in wide)	3.75 in.^{3}

2. MECHANICAL PROPERTIES OF THE I-BEAMS

Standard A.S.T.M. tensile specimens having a gage length of 8 in and reduced section 1½-in wide were cut from one of the beams which was not used in fabricating the floor. One specimen was cut

FIGURE 4.—*Lower surface of the completed floor ready for test.*

FIGURE 5.—*The floor under a nominal load of 420 pounds per square feet of loaded area.*

Deflection at midspan 3¾ inches. After the load had been removed the permanent deflection at midspan was 2¾ inches

from each of the flanges and one from the web of the I-beam. The yield point was taken as that stress under which the specimen showed an extension of 0.002 in. per inch in excess of that computed from Young's modulus of elasticity for the specimen. The results of the tests are given in table 2.

TABLE 2.—*Mechanical properties of the* I-*beams*

Specimen	Yield point	Tensile strength	Young's modulus of of elasticity	Elongation in 8 in
	Lb per sq in	*Lb per sq in*	*Lb per sq in*	*Percent*
Flange	33,600	58,900	30,000,000	27.3
Do	33,700	58,500	30,600,000	27.0
Web	28,900	60,000	29,400,000	28.8

IV. METHOD OF TEST

1. LOADS

Seven equal areas, *R* to *X*, as shown in figure 1, were laid off above each beam by lines drawn midway between the beams and at equal intervals across the beams. The floor was loaded with equal weights of pig iron on each area except the three central areas, *U*, shown shaded in the figure. The center of gravity of the load on each area was approximately over the centroid of the area except that pigs were not piled on the portion of the plate overhanging the outer beams, nos. 1 and 7.

Strain-gage and deflection readings were taken for nominal loads of 40, 80, 100, 120, 140, 160, 180, and 200 lb per sq ft. The actual loads were sometimes greater and sometimes less than the nominal loads. The differences were about 3 lb per sq ft for loads up to 100 lb per sq ft and about 7 lb per sq ft for loads greater than 100 lb per sq ft. The actual loads for each area over each beam were used in the computations.

After the load of 40 lb per sq ft had been applied over the entire floor, the load on area *U* above beams nos. 3, 4, and 5 was not increased when greater loads were applied to the remainder of the floor. This allowed strain-gage readings to be taken on the upper surface of the floor. For loads greater than 200 lb per sq ft when no readings were taken the loads were again applied uniformly to the entire floor.

The floor under a nominal load of 420 lb per sq ft is shown in figure 5. Although the floor would have carried a greater load, it was considered inadvisable to increase the load because the frame, which was a permanent part of the fire-resistance chamber, had deformed considerably. The deflection of the floor at midspan under this load of 420 lb per sq ft was 3⅞ in. This load remained on the floor for 5½ days. After the load was removed, the permanent deflection at midspan was 2¾ in.

2. STRAIN-GAGE READINGS

The locations of the gage lines, all of which were parallel to the beams, are shown in figures 2 and 6.

Two-in gage lines, *A*, *B*, *C*, and *D*, were placed adjacent to the ends and at midspan of beams nos. 3, 4, and 5. These gage lines were designated by the number of the beam followed by *M* for those at midspan and *E* for those adjacent to the end, and finally a letter

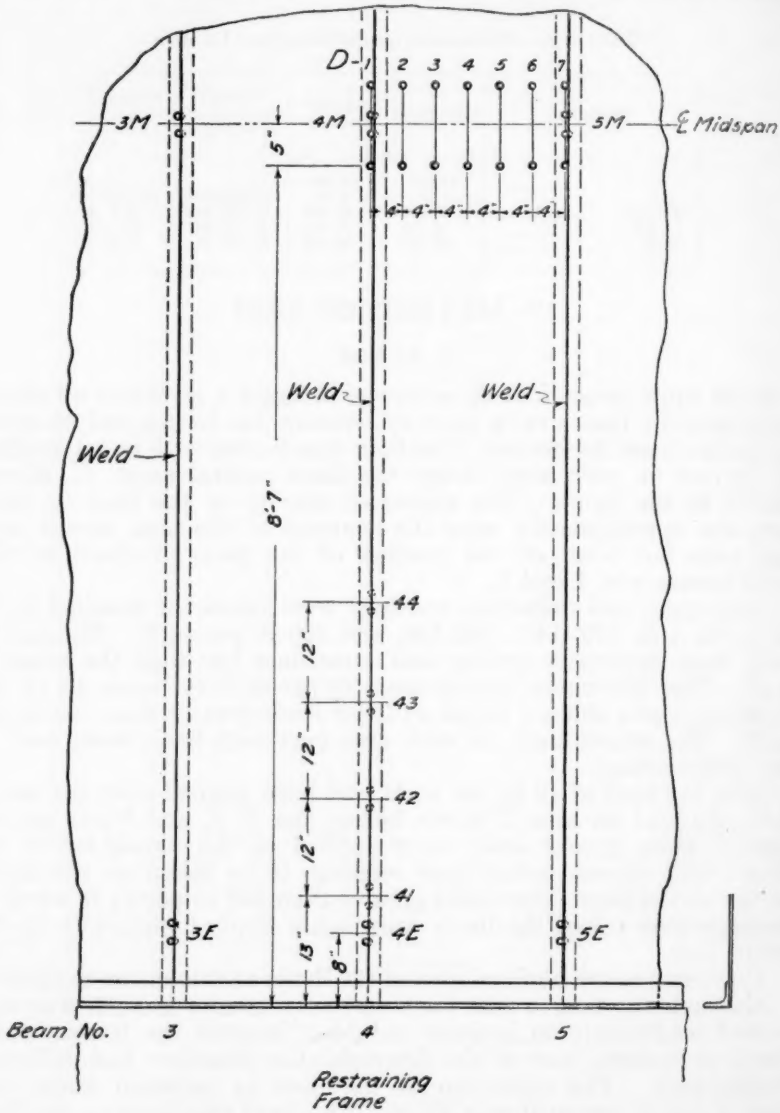

FIGURE 6.—*Location of the gage lines.*

indicating the location on the cross section of the beam element. Gage line *A* was in the middle of the lower flange, *B* and *C* on opposite sides of the web at midheight, and *D* on the upper surface of the plate about ¼ in from the edge of the weld. Thus, gage line 4*EC* was adjacent to the end of beam no. 4 on the side of the web at midheight.

Four additional 2-in gage lines were laid off on the lower flange of beam no. 4. They were spaced 12 in on centers along the beam and were designated 41, 42, 43, and 44.

Seven 10-in gage lines were laid off, longitudinally, at midspan on the upper surface of the floor between beams nos. 4 and 5. These gage lines were spaced about 4 in apart and were designated *D*1, *D*2, *D*3, *D*4, *D*5, *D*6, and *D*7.

Whittemore fulcrum-plate strain gages were used. Each instrument was provided with a "Last Word" dial micrometer reading directly to 0.0001 in. Tenths of a division were estimated. For a Young's modulus of elasticity of 30,000,000 lb per sq in, the stress corresponding to one division on the dial (0.0001 in) was 1,500 lb per sq in for the 2-in instrument and 300 lb per sq in for the 10-in instrument.

3. STRESSES

The stresses obtained from the strain-gage readings were called "measured stresses" to distinguish them from the stresses computed from the dimensions of the floor, the loads, etc., which were called "computed stresses".

The strain (inches per inch) in the floor, caused by change in the loading, was obtained by dividing the difference in the strain-gage readings by the gage length. The measured stress was obtained by multiplying the strain by the Young's modulus of elasticity. The average modulus, 30,000,000 lb per sq in found for the beams was used.

For the 2-in strain gage, it was estimated that, under favorable conditions, the measured stresses might be in error by about 1,000 lb per sq in; for the 10-in strain gage by about 400 lb per sq in.

4. DEFLECTIONS

The deflections of beams nos. 1, 2, 3, and 4 were measured.

A wire was stretched between points on the web of the beam about ¾ in above the lower flange and about 1 in from each end. A mirror having a scale was attached to the web at midspan behind the wire. The scale was graduated in tenths of an inch and the deflection estimated to the nearest 0.01 in. The wire was not placed in the plane of the centroidal axis of the floor because this axis was so close to the lower surface of the plate that it would have been impossible to read the deflection. At the higher loads the plate would have come into contact with the wire. For this test the errors in the deflections due to the location of the wire are believed to be negligible.

V. RESULTS WITH DISCUSSION

1. THE MIDDLE BEAM ELEMENT

The strength and the deflection of a flat steel-plate floor depend upon many things, one of the most important of which is the condition at the ends. In order to simulate the end condition of a floor which is continuous over the supports, the ends of this floor were secured to the frame. The frame, therefore, exerted a negative bending moment on the ends of the floor. Because measuring the negative moment presented unusual difficulties, it was decided to

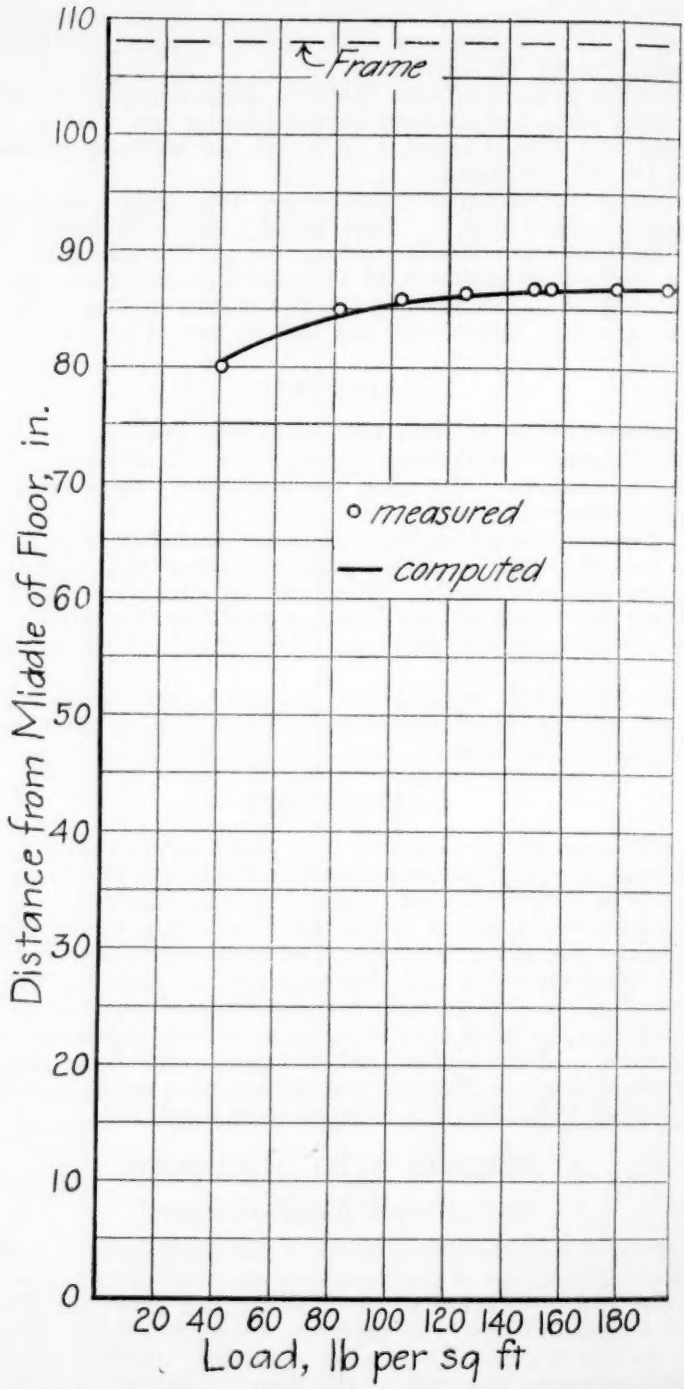

FIGURE 7.—*Movement of the point of zero stress along the bottom flange of beam no. 4 as the load increased.*

determine the point of zero stress in the lower surface of the middle beam from the strain-gage readings on gage lines 41 to 44 with the expectation that this determination, with the other data, would be sufficient to allow the stresses and deflections for the middle beam element to be computed, and that the stresses and deflections in the other beam elements would be approximately the same.

The distance from midspan of the beam was plotted as abscissa and the measured stress as ordinate, and then a faired curve drawn

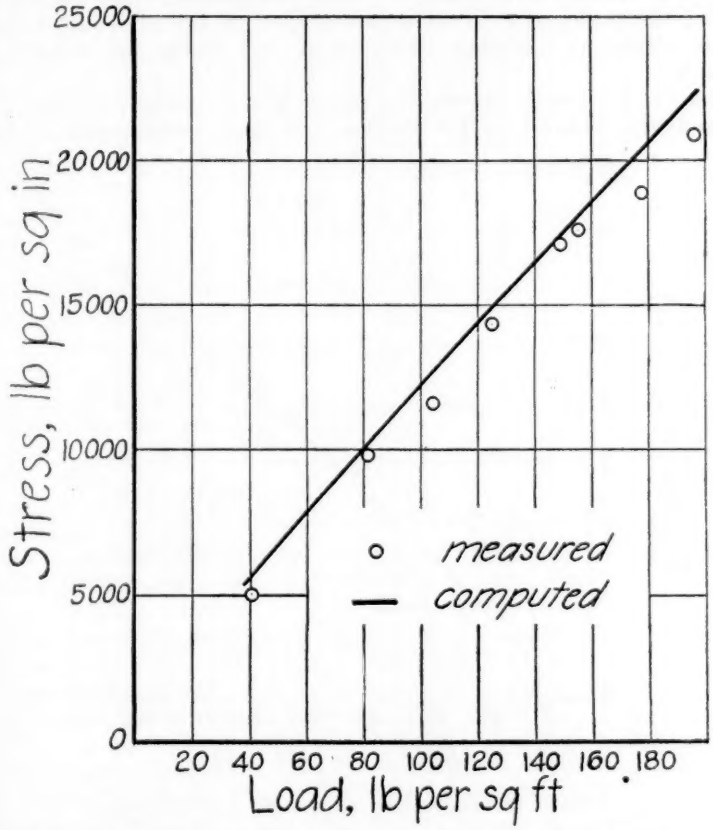

FIGURE 8.—*Stresses in the bottom flange of beam no. 4 at midspan.*

among the points. The point of zero stress was taken where the curve crossed the axis and its distance from midspan of the floor determined. These values are shown in figure 7.

The measured stresses, at gage line *A*, in the bottom flange of beam no. 4 at midspan are shown in figure 8 and the measured deflections in figure 9.

Assuming that there were only vertical forces and negative moments on the ends of the floor it was found that the computed values of the stress on the bottom of beam no. 4 at midspan and of the deflection did not agree with the measured values. Further study led to the belief that the frame might also have exerted tensile forces on the floor. For the middle beam element, assuming that the

entire width of the plate (24 in) was effective, values of the tensile force and the negative moment were found which gave computed values of the stress, the deflection, and the point of zero stress on the lower flange agreeing with the measured values within the errors of observation. These values of the tensile force and the negative moment for each 2-ft width of floor were 7,100 lb and 20,000 lb in, respectively, for a load of 40 lb per sq ft and 12,700 lb and 62,700 lb in, respectively, for a load of 200 lb per sq ft. For intermediate loads the values varied linearly. The computed values for the location of the point of zero stress are shown in figure 7, those for the tensile stress at midspan in figure 8 and those for deflection in figure 9.

Due to the tensile forces the point of zero stress on the bottom flange of the beam does not occur at the same section as the point of

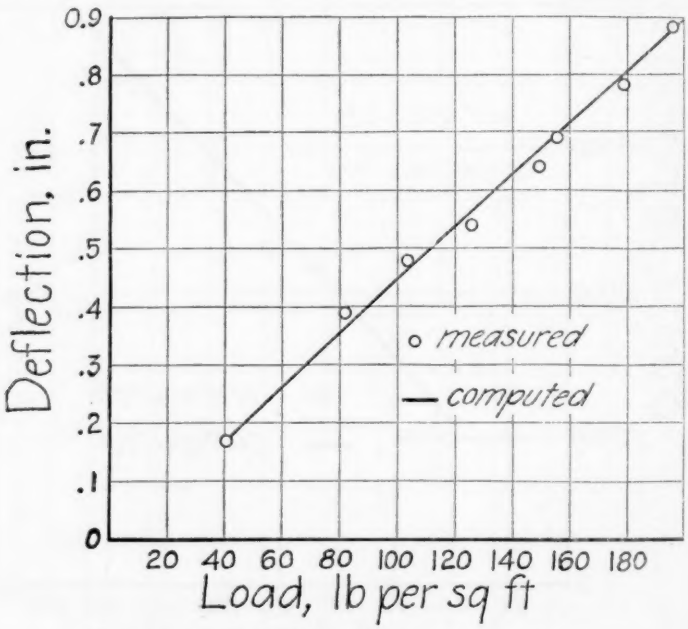

FIGURE 9.—*Deflections of beam no. 4 at midspan.*

inflection. Although the ends of the floor were restrained, the negative moment did not "fix" the ends, i.e., cause the centroidal surface of the beam element to be horizontal at the frame. The computed slope at the ends ranged from 0.0013 for a load of 40 lb per sq ft to 0.010 for a load of 200 lb per sq ft.

2. BEAM ELEMENTS NUMBERS 3, 4, AND 5

The measured stresses at the ends of beam elements nos. 3, 4, and 5 are shown in figure 10 and also the computed values for beam no. 4. The measured stresses at midspan of beam elements nos. 3, 4, and 5 are shown in figure 11 and also the computed values for beam no. 4. The measured values for gage lines *EA*, *EB*, *EC*, *MA*, *MB*, and *MC*, which were below the plates, are consistent within the error of the strain-gage readings but are greater than the computed values for

beam no. 4. Those for *EA* on the bottom flange of the beam are greater than the computed values, probably because the lower flange was welded to the frame near these gage lines.

The measured values of the stresses in the upper surface of the plate, gage lines *ED* and *MD*, are very erratic, probably because these gage lines were on the top of the plates and it was impossible to keep the gage holes clear although they were cleaned frequently. Sand and scale dropped from the pigs when the load on the floor was increased and a strong breeze blew through the building. Rain water collecting on the top of the floor also added to the difficulty of obtaining accurate strain-gage readings on the upper surface.

Beam elements nos. 3, 4, and 5 were similarly loaded with pig iron, but beams nos. 3 and 5 probably carried a somewhat heavier load due to the action of the adjacent beams nos. 2 and 6 which did not have the reduced load on area *U*.

The measured deflections at midspan for beam elements nos. 1, 2, 3, and 4 are shown in figure 12. The computed values for beam no. 4 are shown in figure 9. That beam no. 2 had the greatest deflection is probably due to the fact that beams nos. 1 and 2 did not have the reduced load on area *U*; and that the center of gravity of the load on beam no. 1 was between beams nos. 1 and 2.

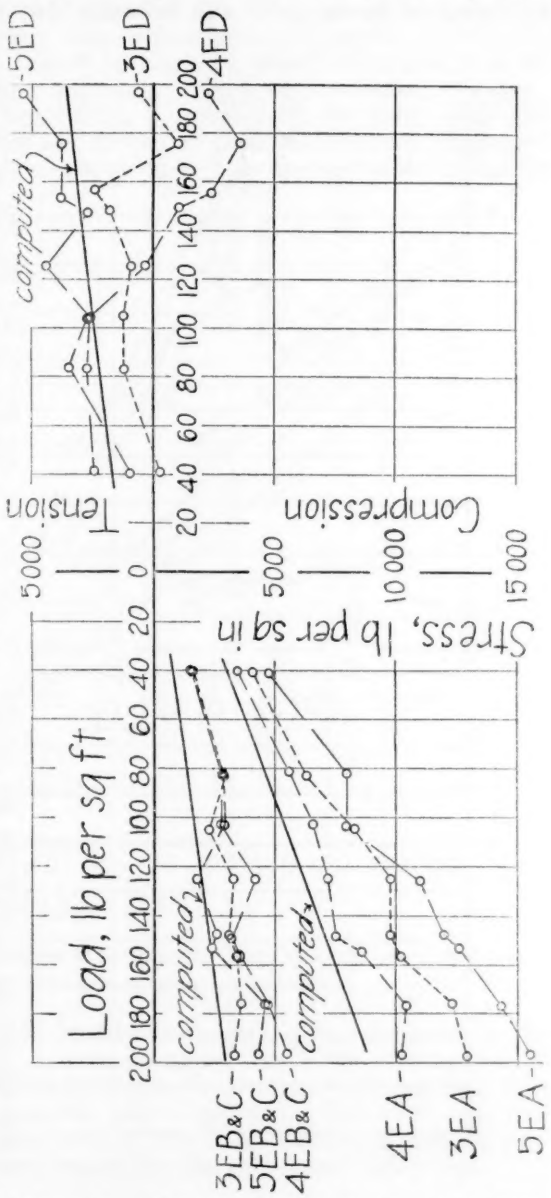

FIGURE 10.—*Measured stresses at the ends of beam elements nos. 3, 4, and 5.*
The computed values are for beam element no. 4.

The actual load on beam no. 1 was therefore somewhat less and that on beam no. 2 somewhat more than the nominal load. The deflection of beam no. 3 was between that of beams nos. 2 and 4

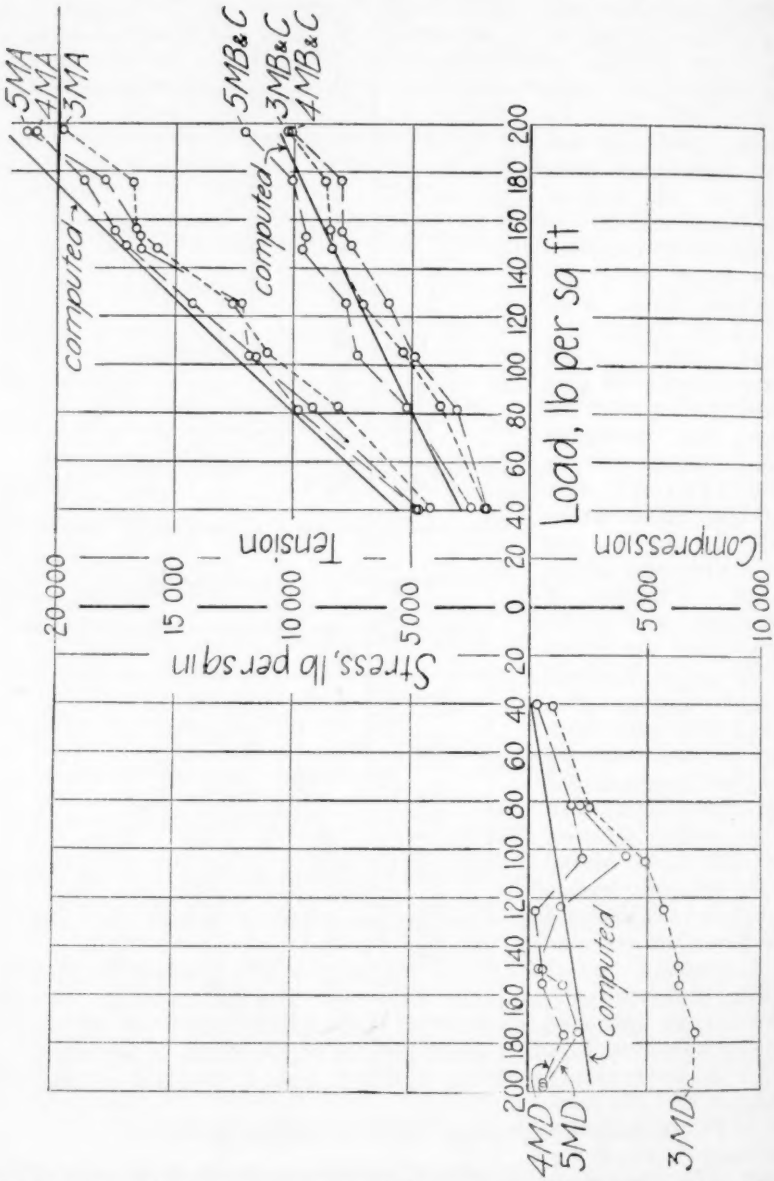

FIGURE 11.—*Measured stresses at midspan of beam elements nos. 3, 4, and 5.*

The computed values are for beam element no. 4.

indicating that the deflection of a beam is dependent not only upon the load on that beam element but is affected somewhat by the loads on adjacent beams by a partial transfer of loads through the plates.

In making all of these computations, it was assumed that the full width of the plates was effective in carrying the load. The results of the computation gave no indication that this assumption was not justified, nor was there any unquestionable experimental evidence to support the assumption (figure 13, showing the distribution of stress across the plate adds some support). Kármán [1] indicates, however, that under conditions not unlike those of the test floor, with the exception that the beams are spaced at infinite distances instead of 24 in, an effective width of about 40 in may be expected unless the

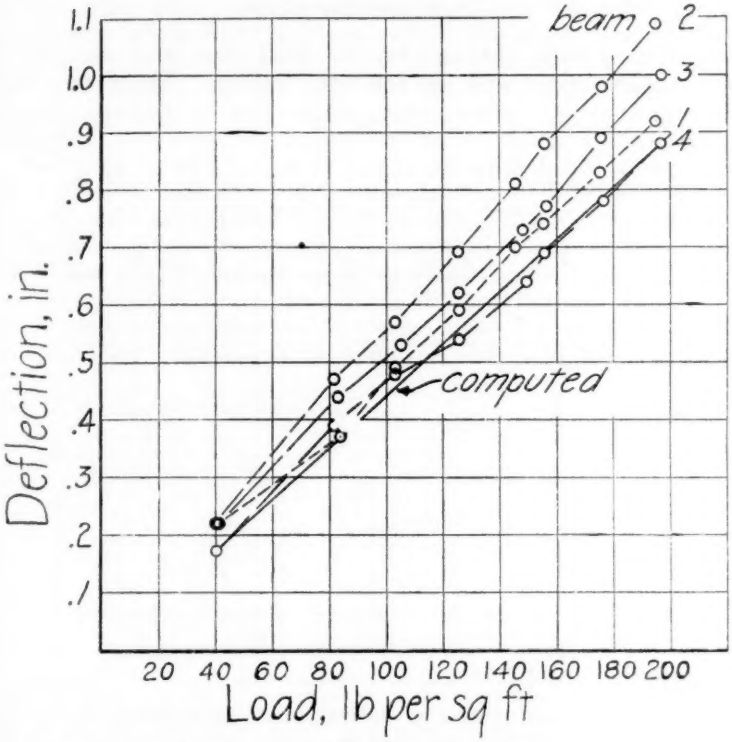

FIGURE 12.—*Measured deflections at midspan for beam elements nos. 1, 2, 3, and 4*
The computed values are for beam element no. 4.

plate is so thin that it will buckle (no buckling was observed in the plates of the test floor). It may be noted that if the effective width were only 8 in instead of the full 24 in, the section modulus, and thus the strength would be reduced only 5 percent. However, the moment of inertia of the cross section would be reduced almost 20 percent, which would increase materially the calculated deflections.

3. THE PLATES

The measured longitudinal stresses in the plate between beams nos. 4 and 5 are shown in figure 13. Computed values for the gage lines over the beams ($D1$ and $D7$) are shown in figure 11, gage lines

[1] Die mittragende Breite, Beiträge zur technischen Mechanik und technischen Physik, p. 114, Julius Springer, Berlin, 1924.

4*MD* and 5*MD*. The values are erratic, presumably due to difficulty in maintaining clean gage holes. Those for *D*6 were especially unsatisfactory. The measured stresses for the nominal load of 180 lb per sq ft were for all gage lines greater than those for the nominal load of 200 lb per sq ft. No reasonable explanation of this inconsistency was found. Making allowance for the errors in these measured stresses, the average stress near the middle of the plate between the beams was somewhat lower than the average measured stress over the beams.

4. THE ASSUMPTIONS

None of the results obtained on this steel plate floor indicate that the assumptions 2 (a) and (b) are not justified. The floor behaves

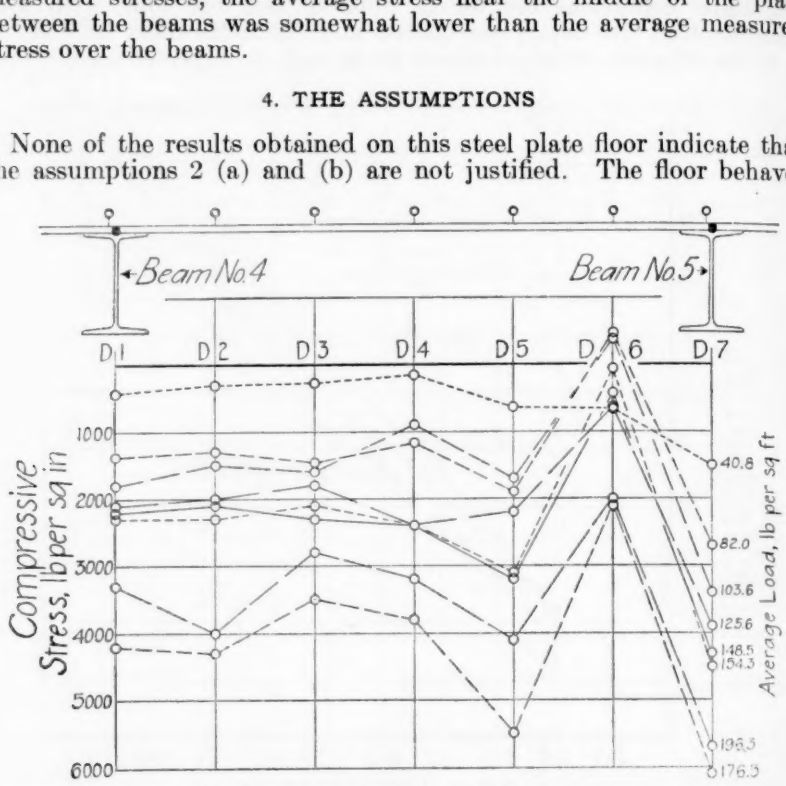

FIGURE 13.—*Longitudinal stresses at midspan in the plate between beams nos. 4 and 5.*

The computed values for *D*1 and *D*7 are shown in figure 11, gage lines 4*MD* and 5*MD*.

as a unit when loads are applied. There was no visible evidence that the welds joining the beams and plates were either ruptured or permanently deformed. The measured stresses do not indicate that the strength of the welds joining the beams and plates was insufficient to cause the floor to behave as a unit.

There is no indication that the axis of average stress in the floor does not coincide with the horizontal line through the centroid of the cross section of the floor.

The measured stresses and the measured deflections of the floor under load agree within the errors of observation with the computed values, when the moment of inertia and the section modulus were obtained from the nominal dimensions of the floor.

The results of this test on a flat steel-plate floor indicate that for ordinary spans, if the spacing of the beams does not exceed 100 times

the thickness of the plates, the full width of the plates may be considered effective and the methods used by engineers in designing steel beams may be used with satisfactory results when designing battledeck floors.

VI. CONCLUSIONS

The results of a loading test of a battledeck floor of 18-ft span, built of 4-in 7.7-lb per ft rolled steel **I**-beams spaced 24-in and ¼-in rolled steel plates indicated that:

1. The continuous manual welds joining the plates to the **I**-beams made by using bare metallic electrodes (5/32-in diameter) and the direct-current arc-welding process united the plates and the beams so that they behaved as a unit when loads were applied.
2. The measured stresses and the measured deflections were in substantial agreement with values computed by the ordinary theory of beams.
3. This floor carried a load of 420 lb per sq ft for 5½ days without any indication of collapse. The deflection under this load was 3⅞ in. After the load was removed the permanent deflection was 2¾ in.
4. The results of this test gave no positive indication as to the width of the plate which may be considered effective. There is a strong presumption, however, that under conditions of loading and length of span not totally unlike those of the test an effective width up to 24 in may be assumed in designing with ¼-in plate.

WASHINGTON, January 16, 1934.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP663

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PORTABLE DETECTOR FOR RADIUM

By L. F. Curtiss

ABSTRACT

Apparatus, making use of a simple 2-stage vacuum-tube amplifier with small ionization chamber, for detecting lost radium preparations is described. Indications of the approach of the chamber to a preparation appear on a small microammeter mounted in the case of the instrument. With a sensitivity such that 10 mg of radium produces a deflection of 10 microamperes at a distance of 1 meter, a lost preparation of this size can be located in a large room filled with filing cases, apparatus, etc., in less than 10 minutes. Small B batteries and large flashlight cells are used to energize the dry-cell tubes so that the instrument is entirely self-contained and thus can be used in any location. The total weight is 18 pounds.

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I. INTRODUCTION

Hospitals and other institutions using a number of radium preparations ranging from 5 to 25 mg are occasionally confronted with the necessity of finding one when lost or misplaced. These preparations are usually in the form of needles between 1 and 2 millimeters in diameter and 15 to 30 millimeters long. When lost, they are often very difficult to find except by means of their radiation. The gold-leaf electroscope is about the only instrument which has been available up to the present time for this purpose. Although it is simple and can be made easily portable, its use in locating a radium preparation, under the usual conditions met with, is very tedious. To survey completely an ordinary room may require several hours, since the electroscope must be read every few feet, and the charging and reading the rate of fall of the leaf requires about 5 minutes for each position. When it comes to searching out of doors, in garbage cans, sewers, and piles of refuse, as is frequently necessary, a gold-leaf electroscope is far from satisfactory. It occurred to the writer that an easily portable

instrument could be built which would show a steady deflection on a meter, increasing in magnitude as the lost preparation is approached. The time required for a search would thus be greatly reduced and such an instrument could be used effectively by persons without special training in its use, which is not true of the efficient use of the electroscope. This paper describes an instrument which appears to fulfill the requirements, and under actual test has shown that it is possible by its use to locate preparations very quickly.

II. AMPLIFYING CIRCUIT

The resistance-coupled, two-stage, vacuum-tube circuit used is fundamentally the same as that described by the author elsewhere,[1] modified slightly to conform to the requirements of this special application. The wiring diagram for this circuit is shown in figure 1. The 32 tube used in the first stage is mounted in a metal shielding tube with the ionization chamber. The control grid of this tube is connected directly to the central collecting rod of the ionization chamber. This rod is also connected to the metal shield through a resistor, R_1, of about 10^9 ohms resistance.[2] The leads for the filament, plate, screen grid, and ionization chamber are brought through a flexible metal tube to the metal battery case in which a 30 tube used

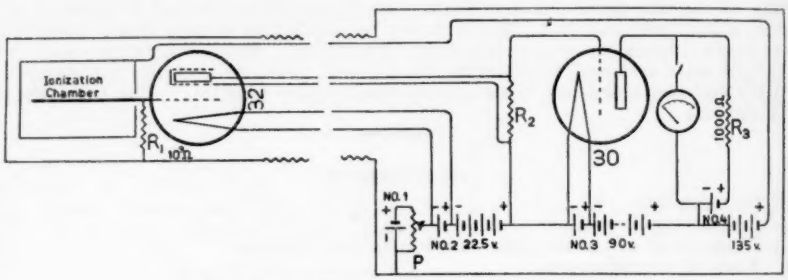

FIGURE 1.—*Wiring diagram of amplifier.*

for the second stage of the amplifier is located, with all batteries for the amplifier. The two stages are coupled through R_2 (a 0.5 megohm resistor), and the output of the last stage is passed through a microammeter shunted by a dry cell, no. 4 in the figure, and a 1,000-ohm resistor R_3, as shown in the diagram. The output current is indirectly controlled by the potentiometer, P, connected with the filament circuit of the first stage. With this arrangement the microammeter will show zero current when adjusted by turning the knob of the potentiometer, P —this being the only adjustment required to make the instrument ready for use. The microammeter will then continue to show zero current until radiation affects the ionozation chamber.

III. DESCRIPTION OF BATTERY CASE AND IONIZATION CHAMBER

As indicated by the wiring diagram, the instrument consists of two parts, an ionization chamber connected by a flexible metal tube to a metal battery case. A cross section, to scale, of the aluminum

[1] Curtiss, L. F., B.S. Jour. Research, vol. 10 (RP 550), p. 585, 1933.
[2] Lacquer-coated graphite resistors described by the author in Rev. Sci. Inst., vol. 4, no. 12, December 1933, have been found to be satisfactory.

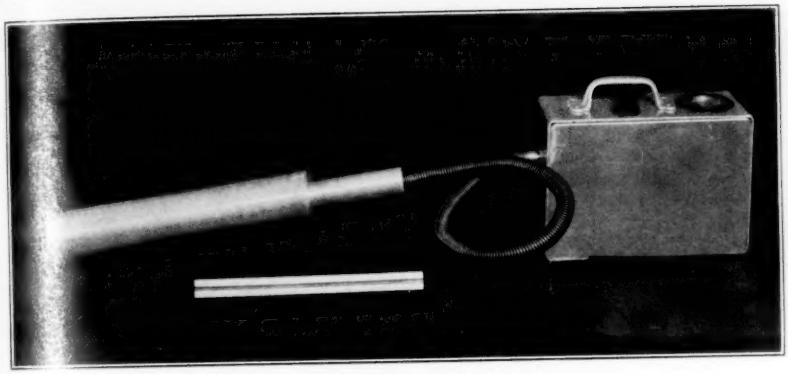

FIGURE 4.—*Photograph of assembled instrument.*

UNIV. OF MICH.

ionization chamber is shown in figure 2.[3] The method of mounting the 32 tube and high-resistance resistor in the metal shielding tube is also shown.

The adopted arrangement permits a very short lead from the collector rod of the ionization chamber to the control grid of the 32 tube, and thus simplifies the problem of electrostatic shielding for this part of the circuit—the only part particularly sensitive to external disturbances.

The battery case, also of aluminum, is shown with one side removed (fig. 3). This drawing, also to scale, shows the position of batteries and other accessories, making evident its compactness. The cells (1.5 volt flashlight cells), chosen for minimum weight, are provided with a spring mounting so that they may be slipped into position and then immediately taken out at the completion of a search—to prolong their life. This, of course, eliminates the necessity for filament switches. The switch shown in the top view is in series with the microammeter which it is intended to protect during the time when the set is momentarily out of use and the dry cells still in position.

A photograph of the actual instrument is shown in figure 4, with a 12-inch scale, which gives an idea of the size. The total weight is

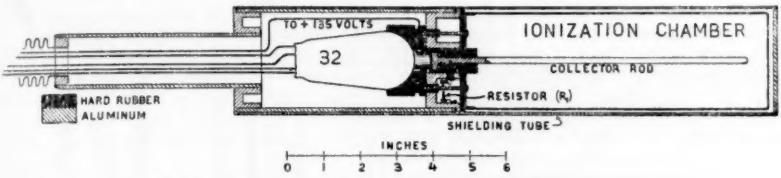

FIGURE 2.—*Cross section of ionization chamber.*

less than 18 pounds. When in use, the battery case is carried in one hand and the ionization chamber in the other. Sufficient flexibility is afforded by the corrugated-metal tube so that the ionization chamber can be pointed in any direction relative to the case.

IV. TESTS OF ARRANGEMENT

To obtain some evidence regarding the effectiveness of the device, representative trials were made in which 10 mg of radium was concealed from view in relatively inaccessible locations unknown to the operator. He was then given the information which might be expected to be available when a preparation is actually lost. First, several trials were made with preparations concealed in backs of filing cases, under trash baskets, etc., in a large room. The only information given was that the preparation was in that room. The average time required to locate the radium was about 5 minutes.

A further trial was made out of doors. A 10-mg preparation was concealed in the roots of grass along the curbing of a roadway connecting two buildings about 500 yards apart. The operator was then

[3] All metal parts are made of aluminum to reduce weight.

conducted over the route taken by the person who had "lost" the preparation. One trip over the route with the instrument, requiring less than 5 minutes, resulted in recovery of the hidden sample. In

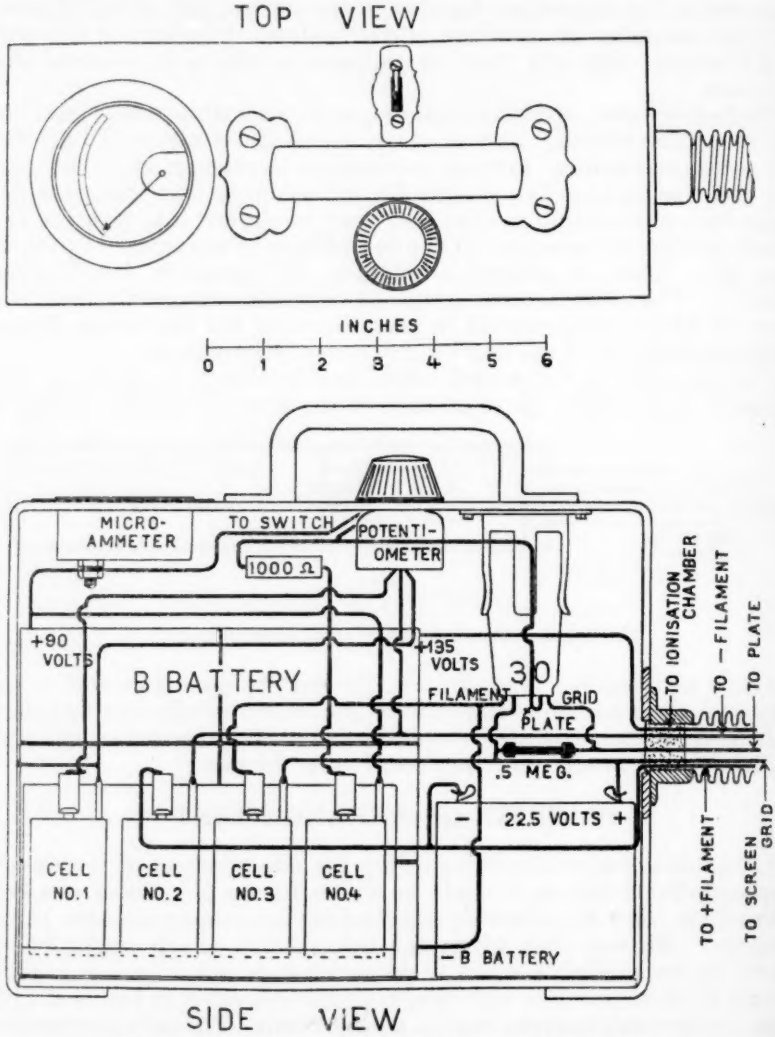

FIGURE 3.—*Drawing showing interior of battery case.*

all tests of this kind, the arrangement proved to have many advantages over the electroscope for this purpose.

The writer wishes to express his indebtedness to B. W. Brown for help in making the apparatus and A. V. Astin for aid in designing the device.

WASHINGTON, December 14, 1933.

U.S. Department of Commerce, Bureau of Standards

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DETERMINATION OF SMALL AMOUNTS OF ZINC IN STEELS AND IRONS

By H. A. Bright

ABSTRACT

A comparison of three procedures for the determination of small amounts of zinc in steels and cast irons was made.

The first procedure, which involved the removal of iron by ammonium hydroxide, was found to be rapid and sufficiently accurate for the usual commercial determinations of zinc over a range of 0.005 to 0.30 percent. The second procedure, in which iron is removed by extraction with ethyl ether, was found to be the most satisfactory for amounts of zinc of the order of 0.001 percent. The third procedure, in which the zinc is precipitated by hydrogen sulphide in the presence of iron, gave satisfactory results with 0.003 percent, or more, of zinc in 15-g samples.

The results of analysis of four representative materials showed that the zinc content of steels and irons is very small, of the order of >0.0005 percent.

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I. INTRODUCTION

As metallurgical science advances, attention is being directed more and more to the effects of small amounts of impurities on the properties of metals. Determination of these impurities, which often occur in very minute amounts, constitutes a special field of analysis, because ordinary methods fail. Although zinc has sometimes been mentioned as a possible constituent of steels and irons,[1] a review of the literature shows but little information on methods for its determination in these materials.

The chief difficulty in any method for the determination of zinc in steel lies in the separation of the minute amount of zinc from the

[1] C. E. Williams and J. D. Sullivan state that zinc, if present in open-hearth steel, exists in very small amounts, probably less than 0.001 percent; cf. "Residual Metals in Open-Hearth Steel", Metals and Alloys, vol. 3, p. 240, 1932, and vol. 4, p. 151, 1933.

large amount of iron. In Ibbotson's method for determining zinc in iron ores,[2] zinc is precipitated as the sulphide from a sulphate solution in which the proper acidity has been obtained by adding ammonium formate and formic acid. In a few tests of this method made by the author satisfactory separations were not obtained in solutions containing 0.5 mg of zinc and 5 to 10 g of iron, probably because of failure to obtain the correct pH for precipitating zinc sulphide. Lundell, Hoffman, and Bright[3] suggest that extraction of ferric chloride by ethyl ether may possibly yield the best results in separating small amounts of zinc from large amounts of iron. Hills[4] recommends precipitation by hydrogen sulphide in a hydrochloric acid solution adjusted to the optimum pH by the addition of sodium citrate and citric acid. In a method for testing ferric chloride for zinc (maximum limit 0.01 percent of zinc), the Committee on Reagents of the American Chemical Society[5] recommends that zinc and copper be separated from the iron by pouring a neutral, or slightly acid, solution of ferric chloride slowly into a relatively large amount of ammonium hydroxide. The mercury cathode, so often a useful tool in analytical chemistry, is not applicable in this problem because zinc, as well as iron, is deposited in the mercury. Neither is the mercuric sulphocyanate method of Lundell and Bee[6] suitable, because precipitation of zinc is always incomplete in the presence of large amounts of iron.

It appeared advantageous, therefore, to investigate the three applicable methods of separation, namely—ammonium hydroxide, extraction with ether, and hydrogen sulphide—as to their suitability for use in the determination of such amounts of zinc as may occur in steel, and, if possible, to develop complete procedures for the determination of this element in steels and irons. It was also planned to make a survey of the zinc content of the Bureau's standard samples of steel and iron. This was abandoned when analyses of four representative samples indicated that if normal steels and irons contain any zinc, the amount must be very small—of the order of <0.0005 percent.[7]

II. EXPERIMENTAL PROCEDURE

Of the separations that have been outlined, three—precipitation by ammonium hydroxide, extraction with ethyl ether, and precipitation by hydrogen sulphide—were tested on solutions of certain steels by themselves and with added amounts of zinc. All of these separations leave zinc with certain other elements, such as copper and molybdenum, which must be removed before the final precipitation of zinc. These elements are removed best by precipitating with hydrogen sulphide in solutions of moderate acidity (2.5 percent). Zinc can then be determined in the filtrate by precipitation as the sulphide in 0.01 *N* acidity[8] followed by ignition of the filtered sulphide to oxide.

[2] F. Ibbotson, The Chemical Analysis of Steel Works' Materials, p. 229. Longmans Green & Co., London, 1920.

[3] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, "Chemical Analysis of Iron and Steel", p. 387, John Wiley & Sons, New York, 1931.

[4] F. G. Hills, Anal. Ed. Ind. Eng. Chem., vol. 5, p. 201, 1933.

[5] Anal. Ed. Ind. Eng. Chem., vol. 4, p. 154, 1932.

[6] G. E. F. Lundell and N. K. Bee, Trans. Am. Inst. Metals, vol. 8, p. 146, 1914.

[7] The complete, or nearly complete, absence of zinc can probably be attributed to the relatively low boiling point of zinc (906 C), a temperature considerably below the melting point of iron or steel, and to the ease with which it is oxidized in the furnace or cupola.

[8] The best precipitation of zinc sulphide is obtained in a sulphuric acid-sulphate solution, cf. "Applied Inorganic Analysis." Hillebrand and Lundell p. 331, John Wiley & Sons, New York, 1929.

Descriptions of the procedures for the three methods investigated are given in the following sections, II 1, 2, and 3. In all cases blanks were carried through all operations and deducted before calculation of the amount of zinc found.

Obviously zinc-free glassware, pyrex for example, must be used if determinations of minute amounts of zinc are in question. Furthermore, the use of a rubber policeman is to be avoided unless it is known to be free from zinc.

1. PRECIPITATION WITH AMMONIUM HYDROXIDE

In the ammonium hydroxide method the sample is dissolved in sulphuric acid, the solution poured slowly into a considerable excess of ammonium hydroxide, and filtered. The filtrate is boiled to remove most of the ammonium hydroxide, made slightly acid (about 2.5 percent by volume) with sulphuric acid, and treated with hydrogen sulphide to precipitate members of the hydrogen sulphide group, such as copper and molybdenum. The solution is again filtered, the filtrate boiled to remove hydrogen sulphide, and the acidity adjusted to 0.01 *N*. The zinc is then precipitated as the sulphide which is ignited to the oxide.

(a) PROCEDURE

Transfer 5 g (if the zinc content exceeds 0.05 percent use 1 to 2 g) of the sample to a 400-ml pyrex beaker, add 30 ml of diluted sulphuric acid (1+3)[9] and 75 ml of water. Cover, and heat gently, with occasional shaking, until reaction ceases. (With cast irons, or high molybdenum steels, filter at this stage through a rapid paper and wash several times with warm water.) Cool slightly and add 50 ml of a freshly made 20 percent solution of ammonium persulphate (not less than 85 percent purity). Boil the solution about 8 minutes. If manganese dioxide is precipitated add sulphurous acid, drop by drop, until the solution clears.

Boil for about 2 minutes, dilute to 200 ml and pour the warm solution (70 to 80 C) slowly and while stirring into 95 ml of diluted ammonium hydroxide (25 ml water + 70 ml of ammonium hydroxide + 4 g of ammonium sulphate)[10] contained in a 400-ml beaker. Let settle for a few minutes and filter, by suction, through a large rapid paper, or Büchner funnel, and wash once with a diluted solution of ammonium hydroxide (1+25, containing 2 g of ammonium sulphate per liter). If the zinc content exceeds 0.03 percent the precipitate should obviously be washed several times.

Boil the filtrate until the volume has been reduced to about 150 ml. Add 2 drops of methyl orange (0.1 percent), treat with diluted sulphuric acid (1+1) until the color changes to red and then add 7.5 ml. of the acid in excess. Pass hydrogen sulphide through the solution for about an hour, let settle for 15 to 20 minutes and filter through a tight paper. (With molybdenum steels, the solution shoud be heated to about 75 C and maintained at that temperature during the passage of hydrogen sulphide.) Wash the precipitate a few times with a diluted solution of sulphuric acid (1+99) containing hydrogen sulphide.

Boil the filtrate until hydrogen sulphide has been expelled (10 to 15 minutes) and cool to 20 C. (With molybdenum steels a small

[9] The symbol (1+3) indicates here, and throughout this paper, one volume of the concentrated acid sp gr 1.84 diluted with three volumes of water.

[10] Ammonium sulphate is not as necessary with small as with large amounts of zinc, but is added because it involves no great trouble or expense and will take care of the exceptional case, cf. E.G.R. Ardagh, Ind. Eng. Chem., vol. 16, p. 298, 1924, who uses a similar solution for washing ferric hydroxide precipitates free from zinc.

precipitate may result at this stage and should be removed by filtration.) Add two drops of methyl orange solution, and then ammonium hydroxide (filtered) until the solution just turns yellow. Add *N* sulphuric acid until the yellow color changes to orange and then add 1.0 ml for each 100 ml of solution. The volume of solution at this point should be about 150 to 175 ml and the strength of the acid and the amount added must be carefully watched in order that the solution shall not be more acid than 0.01 *N*. Cool to room temperature, and pass a rapid current of hydrogen sulphide through the solution for 60 minutes. Let stand for at least 3 hours and filter through a small tight paper, containing a little paper pulp. Wash 10 to 12 times with cold water. Char the paper and precipitate at a low temperature in a small weighed porcelain crucible, burn the carbon at as low a temperature as possible (without flaming) and then gradually raise the temperature to 900–950 C.[11] Cool in a desiccator and weigh. Subtract the blank obtained for the whole series of operations, and calculate the percentage of zinc.[12] The results obtained by this method are given in table 1.

TABLE 1—*Determination of zinc in steels and irons*

[Separation of iron by precipitation with ammonium hydroxide]

Material and weight of sample used	Zn added	ZnO obtained	Percentage of zinc		Error
			Added	Found	
	mg	*mg*			*Percent*
5 g of steel 8d [1]	0.25	0.2	0.005	0.003	−0.002
5 g of steel 8d	.25	.3	.005	.005	.000
5 g of iron 107	.3	.3	.006	.005	−.001
5 g of steel 8d	.5	.7	.01	.011	+.001
5 g of steel 65a	.5	.6	.01	.010	.000
5 g of iron 107	.5	.6 [2]	.01	.010	.000
5 g of iron 107	.5	.5	.01	.008	−.002
5 g of steel 8d	3.0	3.2	.06	.051	−.009
1 g of steel 8d	2.0	2.5	.20	.20	.00
1 g of steel 8d	3.0	3.7	.30	.29	−.01

[1] Compositions: no. 8d, bessemer steel, C=0.078, Mn=0.482, Si=0.018, Cu=0.013, Ni=0.004, Cr=0.007, V=0.003, Mo=0.003, Sn=0.002, As=0.007; no. 65a, acid electric steel, C=0.258, Mn=0.748, Si=0.441, Cu=0.176, Ni=0.242, Cr=0.178, V=0.006, Mo=0.005, Sn=0.024, As=0.012; no. 107, nickel-chromium-molybdenum cast iron, C=2.57, Si=2.34, Cu=0.074, Ni,=0.807, Cr=0.455, V=0.015, Mo=0.687, As=0.01.

[2] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

2. EXTRACTION WITH ETHYL ETHER

In the ether method most of the iron is separated from the zinc by treating a hydrochloric acid solution of the sample with ethyl ether.[13] The extracted acid solution is then treated with sulphuric and nitric acids, evaporated to fumes of sulphuric acid, diluted, and poured into ammonium hydroxide. From this point the procedure is the same as described for the ammonium hydroxide method, II, 1 (a).

[11] Zinc oxide is very slightly volatile at 1,000 C. Zinc will be volatilized and lost as metal at lower temperatures if carbon still remains. If the ignited oxide is not of normal appearance (yellow when hot and white when cold), it must be dissolved in diluted sulphuric acid and both precipitations with hydrogen sulphide repeated.

[12] If the net weight of the ignited precipitate is less than 0.2 mg, the amount of zinc is best estimated nephelometrically by the ferrocyanide method as follows: Dissolve the ignited oxide in 20 ml of diluted hydrochloric acid (1+9) and transfer to a Nessler tube. Add 0.1 g of potassium chloride and dilute to exactly 50 ml. Add exactly 1 ml of a freshly prepared 2 percent solution of potassium ferrocyanide. Shake and compare in a few minutes with a series of suitable standards (e.g., 0.05, 0.10, 0.20 mg of zinc) prepared at the same time and in exactly the same manner. To obtain good results by the nephelometric method it is essential that unknown and standards be treated exactly alike. For further details see "The Nephelometric Analysis of Zinc." L. T. Fairhall and J. R. Richardson. Jour. Am. Chem. Soc., vol. 52, p. 938, 1930.

[13] $ZnCl_2$ is reported by F. Mylius and C. Hüttner, Ber., vol. 44, p. 1315, 1911, as being slightly extracted (0.2 percent) by ether. With the small amounts of zinc involved in this investigation, this factor is negligible.

(a) PROCEDURE

Transfer 25 g of sample to an 800-ml pyrex beaker and add 200 ml of diluted hydrochloric acid (3+1). Cover and heat gently, with occasional shaking until reaction ceases. (With cast irons cool, dilute to 250 ml, allow carbonaceous matter to settle, filter through a rapid paper and wash several times with water.) Oxidize the ferrous iron by slowly adding about 30 ml of diluted nitric acid (1+1) and gradually heating to boiling. The oxidizing action is apt to be quite rapid, in which case it should be checked by momentarily immersing the beaker in cold water. Boil or evaporate the solution until the volume has been reduced to about 50 ml, add 30 ml of hydrochloric acid and again evaporate to a volume of about 50 ml. Add 250 ml of diluted hydrochloric acid (sp gr 1.11) and cool the solution to room temperature. Transfer to a liter separatory funnel, cool the container and contents to 5 C and add 550 ml of cp ethyl ether.[14] Carefully shake the funnel for a few minutes and then allow the two layers to separate for about 10 minutes. Draw off the lower (acid) layer into the original 800-ml beaker. Warm the extracted acid portion on a steam bath until free from excess ether and then boil down to a volume of about 50 ml. Add 14 ml of diluted sulphuric acid (1+1) and 15 ml of nitric acid (spgr 1.42) cover, and boil for a few minutes. Remove the cover glass, evaporate to fumes of sulphuric acid, and continue the fuming for a few minutes.

Cool, add 100 ml of water, heat until salts are dissolved and pour the warm solution (70 to 80 C) into 100 ml of diluted ammonium hydroxide (1+1), containing 5 g of ammonium sulphate. Filter, wash the precipitate, and treat the filtrate as in method II, 1 (a). The results obtained by this method are given in table 2.

TABLE 2.—*Determination of zinc in steels and irons*

[Separation of iron by extraction with ether]

Material and weight of sample used	Zn added	ZnO obtained	Percentage of zinc	
			Added	Found
	mg	*mg*		
50 g of steel 8d [1]		0.1		[2] <0.0001
25 g of steel 65a [3]		0		
25 g of steel 65a		0		
25 g of steel 22b [3] [4]		0		
50 g of iron 107 [1]		0.1		[2] .0001
50 g of steel 8d [1]	0.50	0.4	0.0010	.0006
25 g of steel 8d	.50	.5	.0020	.0016
25 g of steel 65a	.50	[5] .6	.0020	.0019
25 g of iron 107	.50	[5] .7	.0020	.0022
25 g of steel 8d	2.50	2.6	.0100	.0083

[1] Ether extracted solutions of two 25-g samples combined.
[2] Estimated nephelometrically.
[3] Spectroscopic examination of this steel by W. F. Meggers, Bureau of Standards, showed no evidences of the presence of zinc.
[4] No. 22b, Bessemer steel, C=0.674, Mn=0.935, Si=0.123, Cu=0.009, Ni=0.003, Cr=0.003, V=0.005, Mo=0.002, Sn=0.004, As=0.004.
[5] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

[14] The ether supplied in tin cans was found to contain detectable amounts of zinc, probably originating from the soldering flux used in fabricating the containers. In the work described herein anhydrous ether, analytical reagent quality, was used.

3. PRECIPITATION WITH HYDROGEN SULPHIDE

In this method the sample is dissolved in diluted sulphuric acid (1+5) and filtered. The acidity of the solution is adjusted to about pH 2.5 by the use of a citric acid-sodium citrate solution,[15] and zinc together with other precipitable sulphides is precipitated by hydrogen sulphide. The precipitated sulphides are filtered, washed, and then digested with diluted sulphuric acid (1+9) After filtration, any members of the hydrogen sulphide group still remaining in the solution are removed, and then zinc is precipitated as sulphide as in II, 1 (a).

(a) PROCEDURE

Transfer 15 g of sample to a 500-ml pyrex erlenmeyer flask and add exactly 96 ml (6 ml for each gram of sample plus 6 ml in excess) of diluted sulphuric acid (1+5) Cover with a watch glass and heat gently. When action ceases, filter through an 11-cm rapid paper into a 600-ml pyrex beaker, and wash several times with warm water.

Dilute the filtrate to 450 ml, add 5 g of ammonium sulphate, 60 ml of citrate solution (20 g of citric acid and 450 g of sodium citrate dissolved in water, filtered, and diluted to one liter) and stir well.[16] Pass a current of hydrogen sulphide through the solution for 1 hour. Let stand for about 4 hours, or preferably overnight under a bell jar.

Filter through an 11 cm tight paper, containing some paper pulp, and wash a few times with cold water. Return the paper and contents to the original beaker, add 55 ml of diluted sulphuric acid (1+9) and boil gently to expel hydrogen sulphide (10 to 15 minutes). Filter through a 9-cm rapid paper and wash with warm water. Add a few drops of methyl orange solution to the filtrate and neutralize with ammonium hydroxide. Then add sufficient diluted sulphuric acid (1+1) to make the solution about 2.5 percent acid. Treat with hydrogen sulphide, filter through a tight 9-cm paper, and precipitate zinc in the filtrate, etc., as directed in section II, 1 (a). The results obtained by this method are given in table 3.

TABLE 3.—*Determination of zinc in steels and irons*

[Separation of zinc by precipitation with hydrogen sulphide]

Material and weight of sample used	Zn added	ZnO obtained	Percentage of zinc	
			Added	Found
	mg	*mg*		
15 g of steel 8d	0.40	[1] 0.4	0.0027	0.0021
15 g of steel 8d	.40	[1] 0.4	.0027	.0021
15 g of steel 8d	1.00	[1] 1.2	.0067	.0064
15 g of steel 65a	1.00	[1] 1.1	.0067	.0059
15 g of iron 107	1.00	1.1	.0067	.0059
5 g of steel 65a	5.0	6.4	.10	.102
15 g of steel 22b	15.0	19.1	.10	.102

[1] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

[15] The Nephelometric Analysis of Zinc. L. T. Fairhall and J. R. Richardson. Jour. Am. Chem. Soc vol. 52, p. 938, 1930. The Determination of Zinc in Biological Materials, W. R. Tood and C. H. Elvehjem, Jour. Biol. Chem., vol. 96, p. 609, 1932. F. G. Hills, cf. footnote 4, p. 384.

[16] The pH of the solution at this point should be about 2.5 and can, if desired, be checked as follows: Pour about 15 ml of the solution into a small beaker and add two drops of thymol blue indicator (0.04 percent). The solution should be yellow. If red, more citrate must be added. The acidity of the solution is determined in a small portion because the color of the large volume of iron solution is too deep. The test portions are subsequently added to the main solution.

III. SUMMARY

Summarizing the data given in tables 1, 2, and 3, together with observations made during the work, it can be said that, (1) the ammonium hydroxide method is fairly rapid and surprisingly accurate for separating zinc from iron in 5–g samples containing from 0.005 to 0.06 percent of zinc. This procedure should also yield good determinations of zinc in 1–g samples of zinc-bearing iron ores; (2) extraction by ethyl ether appears to be the most suitable method for removing large amounts of iron from very small amounts of zinc, and (3) the hydrogen sulphide method yields satisfactory results with 15–g samples containing 0.003 percent, or more of zinc. A limited number of experiments with this method involving more iron and less zinc were not entirely satisfactory, probably because the proper acidity for the initial sulphide precipitation was not obtained.

The results of analysis of four representative materials showed that the zinc content of steels and irons is very small, of the order of <0.0005 percent.

WASHINGTON, October 31, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP665

Part of Bureau of Standards Journal of Research, vol. 12, March 1934

THERMAL EXPANSION OF BEARING BRONZES

By Peter Hidnert

ABSTRACT

This paper gives data on the linear thermal expansion of cast bearing bronzes (copper-tin and copper-tin-lead alloys) at various temperatures between 20 C (68 F) and 200 C (392 F). The results obtained on heating and cooling are shown in figures 1 and 2. Coefficients of expansion for various temperature ranges are given in table 2. The coefficients of expansion obtained in the second tests are generally higher than those obtained in the first tests. The addition of tin to copper, or lead to copper-tin alloys increases the coefficients of expansion. Equations were derived which show the relationship between the tin content and the coefficients of expansion of cast copper-tin alloys and between the lead content and the coefficients of expansion of cast leaded bronzes with a copper-tin ratio equal to about 7.

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I. INTRODUCTION

Data on the linear thermal expansion of bearing bronzes have been published [1] in 1921. A supplementary investigation on the linear thermal expansion of bearing bronzes was recently undertaken in order to supply a demand for data on various cast bronzes and cast leaded bronzes that have not been investigated previously. Measurements were made of the thermal expansion of these alloys at various temperatures between 20 and about 200 C. The effect of tin in the binary alloys and the effect of lead in the ternary alloys were determined.

Bronze and leaded bronze bearings are found in many types of machines. The comparatively high melting points and strength of these alloys make them more suitable for certain purposes than the weaker and lower melting point white metals. Leaded bronzes find

[1] Hidnert, Thermal Expansion of Copper and Some of Its Important Industrial Alloys, B.S. Scientific Paper 410.

wide applications on railroads, in the automotive industry, and in stationary machinery. Information about the physical properties [2] including thermal expansion, at normal and elevated temperatures which these alloys can safely stand, is therefore important.

The Bunting Brass & Bronze Co., Toledo, Ohio, furnished the samples of bearing bronzes and information about the preparation and the chemical composition. The author wishes to express his appreciation for the cooperation by this company and by C. E. Eggenschwiler, formerly research metallurgist for this company. Acknowledgment is also due to the following members of the staff of the Bureau: H. W. Bearce, W. Souder, H. S. Rawdon, and C. G. Peters for valuable suggestions, to H. S. Krider for assistance during the measurements, and to S. Alpher for aid in the preparation of the figures.

II. MATERIALS INVESTIGATED

Table 1 indicates the chemical composition of the samples of bearing bronzes which were investigated. Each sample was 300 mm in length and 9 mm in diameter. Samples 1472 to 1477, inclusive, were made of virgin materials and the remaining samples from commercial materials. All samples except 1477 were cast between 2,100 and 2,150 F into green sand molds. Sample 1477 was poured at 2,000 F. The melting was done in a gas-fired furnace. Bars from which the samples were cut, were cast in the horizontal position and were gated at the ends of the bars.

TABLE 1.—*Chemical composition of bearing bronzes*

Sample	Chemical composition						
	Copper	Tin	Lead	Nickel	Phosphorus	Zinc	Antimony
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1472	99.20				0.04	0.76	
1473	87.75	12.25			.02		
1474	83.80	11.96	4.22		.02		
1475	77.00	11.08	11.90		.02		
1476	69.82	9.72	20.50		.02		
1477	65.40	7.75	26.62	0.25		None	Trace
1478	95.70	1.95	2.32		.03		
1479	75.86	11.57	12.00	.20	.04	.25	0.15
1480	80.02	9.58	9.45	.15	.04	.60	.15
1481	82.28	6.70	7.48	.15	.05	3.20	.15
1482	88.63	8.58	2.08	.25		.34	.15
1483	86.75	9.97	.53		.03	2.75	
1484	73.00	4.45	21.79	.35	.05	.25	.15

III. APPARATUS

The apparatus described in B.S. Scientific Paper 410 was used for the determinations of linear thermal expansion.

IV. RESULTS

Observations were made on the linear thermal expansion of the bearing alloys at various temperatures between 20 and about 200 C. The results obtained on heating and cooling are shown in figures 1 and 2. The expansion curves are plotted from different origins in order to show the individual characteristics of each curve.

[2] W. M. Corse, Bearing Metals and Bearings, American Chemical Society Monograph No. 53, 1930, gives a history of bearing metals and bearings, literature references from 1900 to 1928, abstracts of selected papers, and tables showing properties of bearing metals.

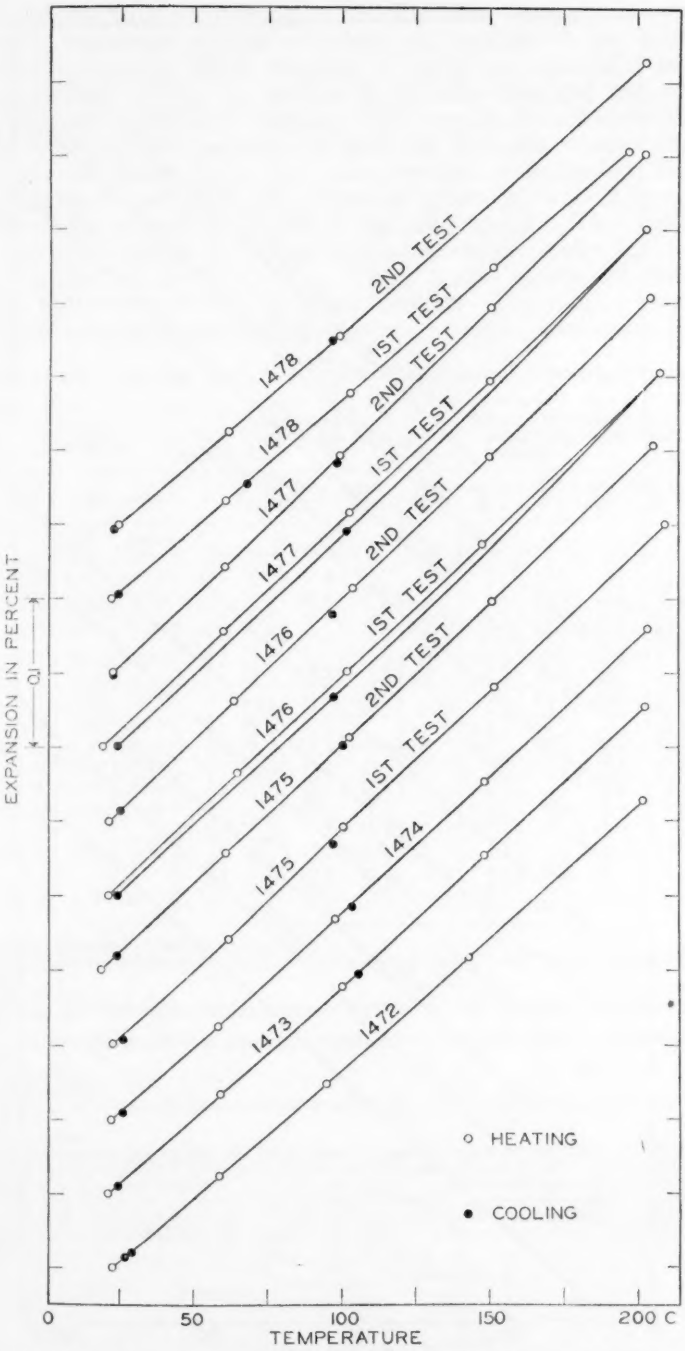

FIGURE 1.—*Linear thermal expansion of cast bearing bronzes (samples 1472 to 1478).*

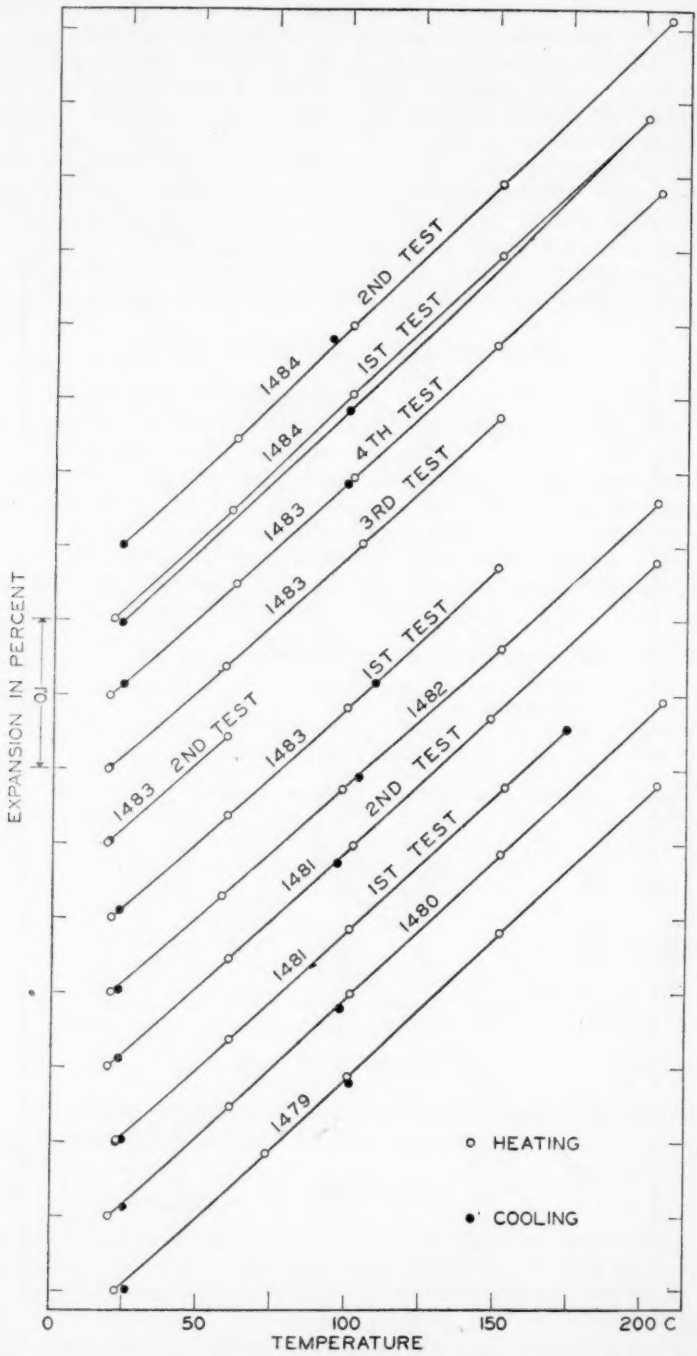

Figure 2.—*Linear thermal expansion of cast bearing bronzes (samples 1479 to 1484).*

The observations on cooling in the first test were, in most cases, below the expansion curves obtained on heating in the first test. Tests were repeated on a number of samples, especially in cases where the observations on cooling in the first test did not lie close to the expansion curve on heating. The results obtained on the first heating apply for cast samples as received, but the results obtained in the second tests apply for heat-treated or annealed samples.

The average coefficients of expansion given in table 2 were computed from the expansion curves in figures 1 and 2. The coefficients of expansion obtained in the second tests are generally higher than those obtained in the first tests. Table 2 also shows the difference in length before and after each expansion test. The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length.[3]

TABLE 2.—*Average coefficients of linear expansion of bearing bronzes*

Sample	Chemical composition [1]			Test no.	Average coefficients of expansion per degree centigrade				Average coefficients of expansion per degree Fahrenheit [2]				Change in length after heating and cooling
	Copper	Tin	Lead		20 to 60 C	20 to 100 C	20 to 150 C	20 to 200 C	68 to 140 F	68 to 212 F	68 to 302 F	68 to 392 F	
	Percent	*Percent*	*Percent*		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	*Percent*
1472 [3]	99.20	------	------	1	16.7	16.9	17.2	17.4	9.3	9.4	9.6	9.6	0.000
1473	87.75	12.25	------	1	17.6	17.7	18.0	18.1	9.7	9.8	10.0	10.1	−.000
1474	83.80	11.96	4.22	1	17.4	17.9	18.1	18.3	9.7	9.9	10.0	10.1	−.002
1475	77.00	11.08	11.90	1	17.7	18.6	18.5	18.6	9.8	10.3	10.3	10.3	−.003
				2	18.4	18.5	18.7	18.8	10.2	10.3	10.4	10.4	.000
1476	69.82	9.72	20.50	[4] 1	18.6	18.6	18.6	18.8	10.4	10.3	10.3	10.4	−.005
				2	18.9	18.9	19.0	19.1	10.5	10.5	10.5	10.6	−.000
1477	65.40	7.75	26.62	[5] 1	19.0	19.0	18.9	19.0	10.6	10.6	10.5	10.6	−.009
				2	18.8	19.1	19.3	19.4	10.5	10.6	10.7	10.8	−.001
1478	95.70	1.95	2.32	1	17.1	17.2	17.3	17.3	9.5	9.5	9.6	9.6	−.001
				2	17.0	17.1	------	17.6	9.4	9.5	------	9.8	.000
1479	75.86	11.57	12.00	1	17.9	18.3	18.6	18.7	10.0	10.2	10.3	10.4	−.005
1480	80.02	9.58	9.45	1	18.0	18.4	18.4	18.6	10.0	10.2	10.2	10.3	−.003
1481 [6]	82.28	6.70	7.48	1	17.7	18.1	18.2	------	9.8	10.1	10.1	------	−.002
				2	17.8	18.0	18.2	18.4	9.9	10.0	10.1	10.2	−.001
1482	88.63	8.58	2.08	1	17.2	17.5	17.6	17.9	9.6	9.7	9.8	9.9	−.003
1483 [7]	86.75	9.97	.53	1	17.6	17.8	18.1	------	9.7	9.9	10.1	------	+.000
				2	17.8	------	------	------	9.9	------	------	------	−.000
				3	17.5	17.8	18.0	------	9.7	9.9	10.0	------	.000
				4	17.6	17.9	18.1	18.3	9.8	9.9	10.1	10.2	−.000
1484	73.00	4.45	21.79	[8] 1	18.4	18.9	18.8	18.8	10.2	10.5	10.5	10.5	−.007
				2	18.7	19.2	19.2	19.2	10.4	10.6	10.6	10.7	.000

[1] See table 1 for complete chemical composition.
[2] The cofficient of expansion per degree Fahrenheit is equal to 5/9 of the coefficient of expansion per degree centigrade.
[3] Zinc 0.76 percent.
[4] On cooling, the average coefficient of contraction is 19.0×10^{-6} between 200 and 20 C and 18.2×10^{-6} between 100 and 20 C.
[5] On cooling, the average coefficient of contraction is 19.5×10^{-6} between 200 and 20 C and 18.8×10^{-6} between 100 and 20 C.
[6] Zinc 3.20 percent.
[7] Zinc 2.75 percent.
[8] On cooling, the average coefficient of contraction is 19.2×10^{-6} between 200 and 20 C and 18.8 $\times^{-6}$ between 100 and 20 C.

[3] After an examination of table 2, C. E. Eggenschwiler made the following comments: "It was especially interesting to observe the rather progressive shortening of the test specimens' length at the end of the first heating, as the lead content increased. Also to note that the second heating tests did not show this condition." He also stated that the results seem to indicate that the alloys are more compact after the first heating. This has been verified by density measurements made by S. Alpher of this Bureau on duplicate samples of 1476, 1477, and 1484, before and after heating to 200 C and cooling to 20 C. The results obtained are as follows:

Sample	Density before heating	Density after heating and cooling
1476 A	9.028 g/cm³	9.031 g/cm³
1477 A	9.362	9.366
1484 A	8.951	8.954

Table 3 shows that the coefficients of expansion of sample 1472 which contains 99.20 percent copper and 0.76 percent zinc, are slightly larger than the coefficients of expansion of electrolytic copper containing 99.97 percent copper. It has been shown in a previous publi-

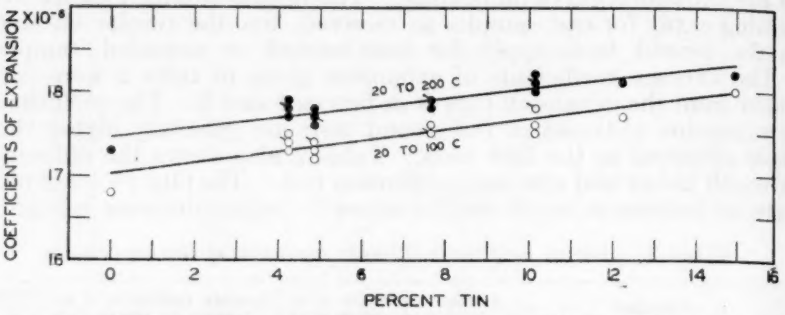

FIGURE 3.—*Effect of additions of tin on the average coefficients of linear expansion of cast copper-tin alloys.*

A tagged symbol indicates more than one value.

cation [4] that the addition of zinc to copper causes an increase in the coefficients of expansion.

TABLE 3.—*Comparison of coefficients of expansion of copper and copper-zinc alloy*

Material	Average coefficients of expansion per degree centigrade			
	20 to 60 C	20 to 100 C	20 to 150 C	20 to 200 C
	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶
Sample 1472, cast copper-zinc alloy	16.7	16.9	17.2	17.4
Electrolytic copper, hot rolled [1]	16.6	16.8	17.0	17.3
Electrolytic copper, hot rolled and drawn [1]	16.6	16.8	17.0	17.2

[1] Hidnert, B.S. Scientific Paper 410.

Table 4 and figure 3 show coefficients of expansion of cast copper-tin alloys. From these coefficients of expansion, the following equations were derived by the method of least squares:

$$_{20}a_{100} = (17.03 + 0.0646\ Sn)\ 10^{-6} \quad (1)$$

$$_{20}a_{200} = (17.47 + 0.0565\ Sn)\ 10^{-6} \quad (2)$$

where $_{20}a_{100}$ represents the average coefficient of expansion between 20 and 100 C, $_{20}a_{200}$ represents the average coefficient of expansion between 20 and 200 C, and Sn represents the percentage of tin. These equations show that the coefficients of expansion of copper-tin alloys increase with increase in the tin content.

[4] Hidnert, B.S. Scientific Paper 410.

TABLE 4.—*Coefficients of expansion of cast copper-tin alloys*

Chemical composition		Average coefficients of expansion per degree centigrade	
Copper	Tin	20 to 100 C	20 to 200 C
Percent	*Percent*	× 10^{-6}	× 10^{-6}
[1] 99.97		16.8	17.3
[2] 95.40	4.25	17.4	17.8
		17.5	17.9
		[3] 17.3	[3] 17.7
		17.4	17.8
[2] 94.86	4.88	17.4	17.7
		17.3	17.7
		17.4	17.8
		17.2	17.6
[2] 92.04	7.67	17.5	17.9
		17.5	17.9
		17.5	17.8
		17.6	17.9
[2] 89.69	10.14	17.6	18.1
		17.5	18.0
		17.8	18.1
		17.8	18.2
[4] 87.75	12.25	17.7	18.1
[4] 84.84	14.95	18.0	18.2

[1] Electrolytic copper, hot rolled. See Hidnert, B.S. Scientific Paper 410.
[2] Four samples (inside and outside sections) cut from casting. See Hidnert, B.S. Scientific Paper 410.
[3] Result on second heating.
[4] Sample 1473, present investigation.
[5] Hidnert, Physical Review, vol. 39, p. 551, 1932.

Figure 4 shows that additions of lead increase the coefficients of expansion of cast bearing bronzes with a copper-tin ratio equal to about 7. The following equations which show the relationship between the coefficients of expansion and the lead content of the bearing alloys were derived by the method of least squares from the data shown in figure 4:

$$_{20}\alpha_{100} = (17.76 + 0.0475\ Pb)\ 10^{-6} \tag{3}$$

$$_{20}\alpha_{200} = (18.16 + 0.0355\ Pb)\ 10^{-6} \tag{4}$$

In these equations, $_{20}\alpha_{100}$ represents the average coefficient of expansion between 20 and 100 C, $_{20}\alpha_{200}$ represents the average coefficient of expansion between 20 and 200 C, and Pb represents the percentage of lead between 0 and 20.50 percent. Table 5 gives coefficients of expansion which were computed from equations (3) and (4).

TABLE 5.—*Effect of lead on the coefficients of linear expansion of cast bearing bronzes with a copper-tin ratio equal to about 7*

Lead	Average coefficients of expansion per degree centigrade	
	20 to 100 C	20 to 200 C
Percent	× 10^{-6}	× 10^{-6}
0	17.8	18.2
4	17.9	18.3
8	18.1	18.4
12	18.3	18.6
16	18.5	18.7
20	18.7	18.9

Figures 5 and 6 show the coefficients of expansion of cast copper-tin alloys and cast copper-tin-lead alloys for the range from 20 to 100 C and from 20 to 200 C, respectively. These figures indicate that the addition of tin to copper, or lead to copper-tin alloys increases the coefficients of expansion. The addition of about 3 percent zinc to two copper-tin-lead alloys (samples 1481 and 1483) does not appear to have an appreciable effect on the coefficients of expansion. With

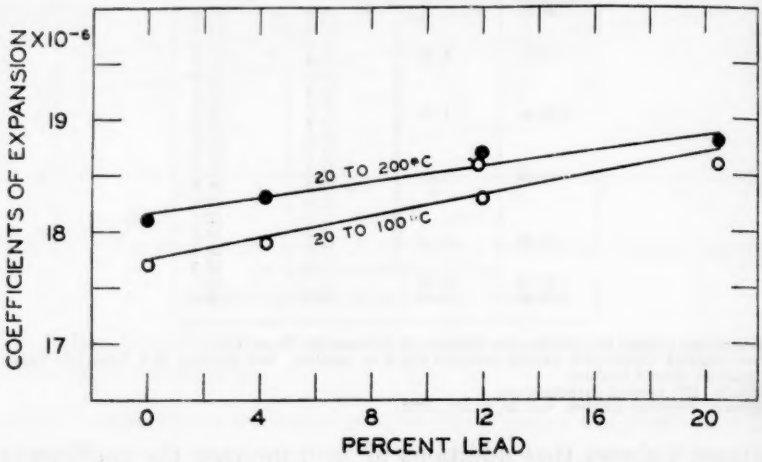

FIGURE 4.—*Effect of lead on the average coefficients of linear expansion of cast bearing bronzes with a copper-tin ratio equal to about 7.*

The tagged symbol indicates the same value for both temperature ranges.

the aid of figures 5 and 6, it is possible to predict the coefficients of expansion of other neighboring alloys that have not been investigated.

V. CONCLUSIONS

1. The expansion curves in the first heating of cast bronzes are in most cases above the observations obtained in the first cooling.
2. The coefficients of expansion obtained in the second heating are generally higher than those obtained in the first heating.
3. The addition of tin to copper, or lead to copper-tin alloys increases the coefficients of expansion.
4. The following equations show the relationship between the tin content and the coefficients of expansion of cast copper-tin alloys:

$$_{20}\alpha_{100} = (17.03 + 0.0646\ Sn)\ 10^{-6}$$
$$_{20}\alpha_{200} = (17.47 + 0.0565\ Sn)\ 10^{-6}$$

In these equations, $_{20}\alpha_{100}$ and $_{20}\alpha_{200}$ represent the average coefficients of expansion from 20 to 100 C and from 20 to 200 C, respectively, and *Sn* represents the percentage of tin between 0 and 15 percent.

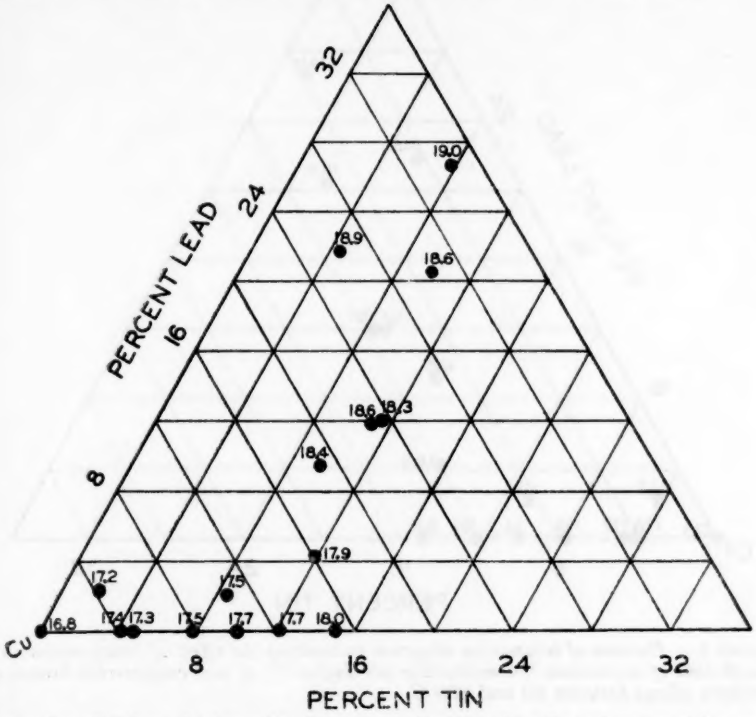

FIGURE 5.—*Portion of triangular diagram indicating the effect of composition on the coefficient of expansion (in millionths per degree C) of cast copper-rich binary and ternary alloys between 20 and 100 C.*

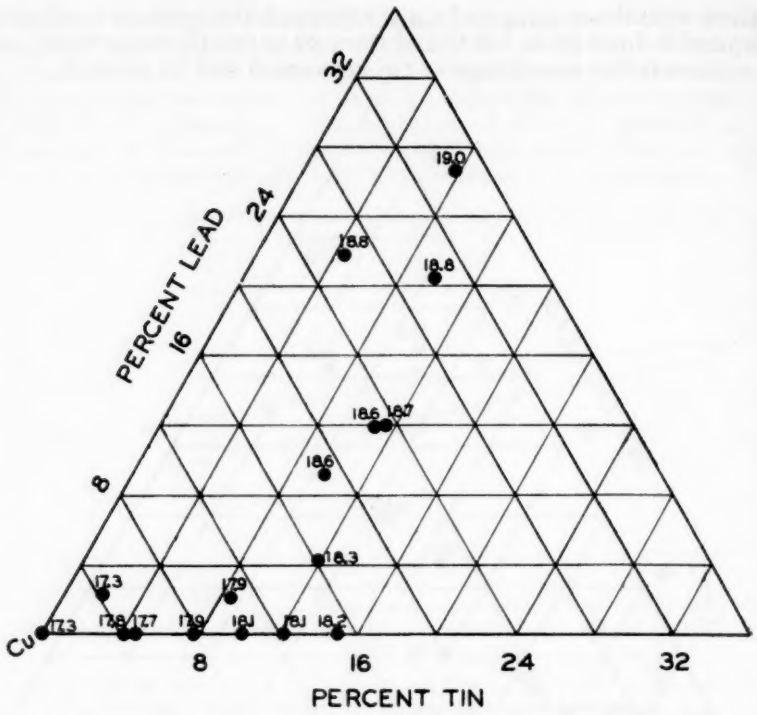

FIGURE 6.—*Portion of triangular diagram indicating the effect of composition on the coefficient of expansion (in millionths per degree C) of cast copper-rich binary and ternary alloys between 20 and 200 C.*

5. The following equations show the relationship between the lead content and the coefficients of expansion of cast leaded bronzes with a copper-tin ratio equal to about 7:

$$_{20}a_{100} = (17.76 + 0.0475\ Pb)\ 10^{-6}$$
$$_{20}a_{200} = (18.16 + 0.0355\ Pb)\ 10^{-6}$$

In these equations, $_{20}a_{100}$ and $_{20}a_{200}$ represent the average coefficients of expansion of leaded bronzes from 20 to 100 C and from 20 to 200 C, respectively, and Pb represents the percentage of lead between 0 and 20.50 percent.

6. With the aid of figures 5 and 6, it is possible to predict the coefficients of expansion of other cast copper-tin and copper-tin-lead alloys.

WASHINGTON, November 14, 1933.

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